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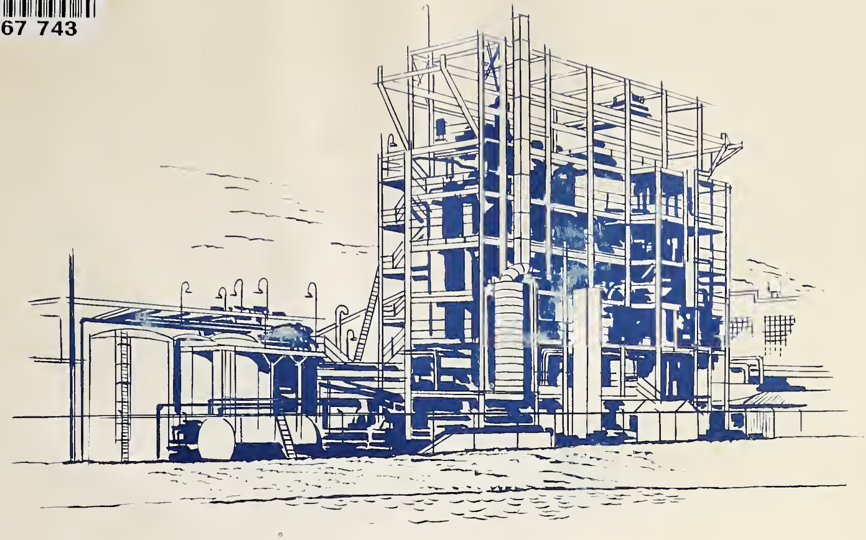

EMULSION POLYMERIZATION OF ACRYLIC MONOMERS

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SPECIAL PRODUCTS DEPARTMENT

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CHAPTER I

SCOPE OF EMULSION POLYMERIZATION

The emulsion polymerization process is a convenient and widely used method for the production of acrylic polymers. This process combines the economy and safety of an aqueous reaction medium with a rapid but readily controlled polymerization reaction to provide high molecular weight polymers in excellent yield and in a form suitable for many applications.

Acrylic polymer emulsions have long enjoyed commercial status; in fact, their usage as base coatings for leather in the 1925-1930 period was the first commercial application of acrylic polymers. They have since been adopted as coatings, finishes, and binders for leather, textiles, and paper, as exterior and interior coatings in home and industry, as adhesives, laminants, elastomers, and floor polishes, and in many other fields of application. The constantly increasing acceptance of these products stems from their versatility and the broad range of their compositions and properties as well as their inherent stability, durability, and pigment-binding characteristics. In many applications, it is advantageous to handle polymers in the form of water-based latexes instead of solutions in hazardous, expensive, odorous, and flammable solvents. In addition, the acrylic emulsion products are readily blended with other typical and desirable components of formulations which may also be supplied as emulsions, dispersions, or aqueous solutions. The earlier acrylic polymers were principally thermoplastic in nature. The utility of acrylic polymers has been extended by the development of thermosetting compositions available in emulsion as well as solution. Thermosetting products are based on copolymers containing functionally substituted acrylic monomers and are characterized by insolubility and extreme durability. Thermosetting of functionally substituted acrylic copolymers can be accomplished by self-curing reactions or by reaction with the functional group of other added substances or polymers.

The purpose of the revised edition of this bulletin is the provision of improved and comprehensive starting point information for the development of polymer emulsions from acrylic monomers. New recipes have been added and methods illustrating the use of newly introduced Rohm and Haas monomers, surfactants, reducing agents, and ion exchange resins are included. The bulletin also offers amplified discussions of process variables, manufacturing equipment, storage and handling recommendations, and evaluation of products.

The Rohm and Haas Company distributes other bulletins on the preparation, properties, and applications of acrylic polymer emulsions. The following are available on request to the Special Products Department:

SPR-243 - The Mechanism of Emulsion Polymerization. I. Studies of the Polymerization of Methyl Methacrylate and n-Butyl Methacrylate.

SP-159 - Catalysts for the Polymerization of Acrylic Monomers.

SP-21 - Hydrosulfites and Sulfoxylates

SPR-250 - Advances in Emulsion Polymerization Technology.

SP-147 - Copolymerization of Monomeric Acrylic Esters.

SPR-227 - Particle Size Technology of Polymer Emulsions. I. Measurement of Particle Size.

SPR-310 - Emulsion Particle Size. I. The Soap Titration of Acrylic Emulsions.

SPR-155 - Film Forming Characteristics of Emulsion Polymers.

SPR-298 - An Apparatus for the Determination of the Minimum Film Temperature of Polymer Emulsions.

SPR-238 - Experimental Study of the Mechanism of Film Formation.

SPR-311 - Mechanism of Film Formation from Latices. Phenomenon of Flocculation.

SPR-235 - Compatibility Studies on Polyacrylate and Polymethacrylate Systems.

SPR-231 - Heterogeneous Polymer Systems. I. Torsional Modulus Studies.

SPR-247 - Relationship of Strain Properties to Empirical Tests.

SPR-157 - Uses and Formulation of Acrylic Emulsion Polymers.

SPR-199 - Acrylic Polymerization Abstracts.

Other publications dealing with specific products will be listed in the appropriate sections of this bulletin.

CHAPTER II

BENCH SCALE METHODS FOR THE EMULSION POLYMERIZATION OF ACRYLIC MONOMERS

The two techniques of emulsion polymerization processes are commonly designated as the "reflux method", in which a water-soluble peroxidic initiator is used, and the "redox method", where peroxide initiators are combined with reducing agents. The directions given here are general for the laboratory preparation of acrylic emulsion polymers. The intent is to present recipes for starting a development program of products based on acrylic polymers. Because of the wide variation in possible polymer compositions, performance requirements, and the effect of the numerous variables on the process, adjustments of reaction conditions and substitutions of minor components may be needed to provide an efficient final process and an acceptable product. Chapter IV will discuss the influence of ingredients and experimental conditions.

These recipes are based on actual laboratory runs. The times of induction periods and exotherms, the peak temperatures, and product data have been taken from these runs and may be considered to be typical; however, a range of similar values would be expected in the hands of other experimenters. The designated weights refer to the amount of each ingredient as supplied. To avoid confusion, the solids content of the Rohm and Haas surfactants furnished as solutions are omitted, but may be found in Chapter IV, Table IV-4.

A. REFLUX METHOD

1. APPARATUS

A typical simple laboratory setup (Figure 1) consists of a 3-neck round-bottom flask fitted with a paddle or propeller stirrer, a reflux condenser, a thermometer, and an addition funnel. The flask is mounted in a water (or oil) bath that can be raised or lowered by a jack; the bath is heated by an immersion heater. A thermometer is suspended in the bath which may also be provided with a stirrer to increase the temperature uniformity of the bath liquid. The power input to the heater is adjusted by a variable transformer. Ordinary laboratory motors with a speed of 300-600 rpm are suitable for small-scale experiments although motors fitted with reducing gears or controlled by rheostats to permit variation of speeds are handy during process studies. For larger operations, it is desirable to use explosion-proof motors, especially when the lower acrylates and methacrylates or other flammable substances are being handled.

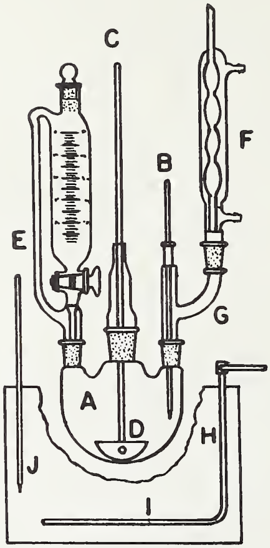
Automatic devices for temperature control are available from suppliers of laboratory equipment. They involve sensing devices attached to the thermometer in the reaction flask or heating bath at a desired scale reading. The temperature is maintained by controlling the electrical input to the heater or by periodically raising and lowering the bath. These devices may reduce the hazard inherent in large-scale operations and permit simultaneous running of several reactions under the control of a single operator. The use of safety shields is also advisable in large runs or in new reactions with unfamiliar reactants. Operations at constant reaction temperature may be carried out by working in a large thermostatted bath.

2. GENERALIZED OPERATING DIRECTIONS

a. In a separate vessel, add the surfactant(s), buffer (if desired), monomer(s), nd initiator(s) in the stated order to about 80 per cent of the water and stir to form an nulsion.

FIGURE 1

REFLUX EMULSION POLYMERIZATION



A	3-Neck Round Bottom Flask
B	Thermometer
C	Stirring Rod and Bearing
D	Stirring Paddle
E	Addition Funnel
F	Reflux Condenser
G	Adapter
H	Heating Bath
I	Immersion Heater
J	Thermometer

b. Place the remaining water and an equal volume of the monomer emulsion in the reaction flask and the rest of the emulsion in the addition funnel.

c. Begin stirring and heating, increasing the temperature until refluxing starts. Boiling usually stops within a few minutes if a low-boiling reactive monomer like ethyl acrylate or methyl methacrylate is being used; the cessation of boiling indicates the consumption of most of the monomer.

d. Gradually add the rest of the emulsion from the addition funnel; for a run with 500-1000 g. of monomer, the addition requires about 1.5 to 2 hours. The rate of reflux is controlled by adjusting the rate at which the monomer emulsion is added and is maintained by the heat of polymerization and the temperature of the bath.

e. When the addition is finished, raise the bath temperature to about 95-97°C. Add a small amount of initiator to ensure complete conversion of monomer and continue heating for 30 minutes to two hours.

f. Cool the emulsion with stirring to a convenient temperature (25-30°C.) and strain through cheesecloth or a screen to remove gums or grit.

B. REDOX METHOD

1. APPARATUS (Figure 2)

Equipment is similar to that used above except that a heating bath is usually not required. However, a gas inlet is normally provided to permit expulsion of air from the flask by passing a slow stream of an inert gas, like nitrogen or carbon dioxide, through the reactants. The addition of inert gas over the surface of the reaction mixture is continued during the polymerization.

2. GENERALIZED OPERATING CONDITIONS

a. Charge the ingredients to the reaction flask in the following order: water, surfactant(s), buffer (if needed), monomer(s), and chain transfer agent (if used). Before adding the other materials, the surfactant(s) should be completely dissolved, warming if necessary. The solution should be at room temperature before adding the monomer(s).

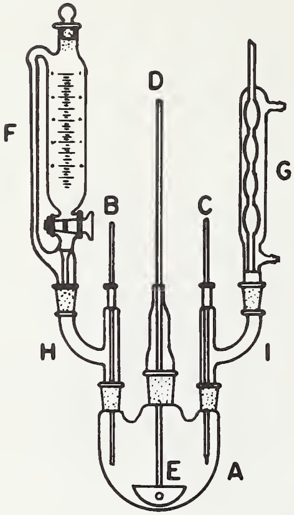
b. Start the passage of inert gas and stir until the air has been expelled from the reaction mixture and vessel and the emulsion is well established; this usually requires 15-30 minutes.

c. Add the components of the redox system in the following order: ferrous salt, persulfate, reducing agent, and, if desired, a secondary initiator at any appropriate temperature from 15 to 45°C. NOTE: The initial temperature must take into account the provisions made for the absorption of heat liberated during the polymerization (See Chapter IV, section A.2.a., pages 31-32). The redox ingredients are usually charged as aqueous solutions.

d. After the initiators have been added, an induction period of 1 to 30 minutes occurs and is followed by a rise in temperature signalling the inception of polymerization. The temperature usually rises rapidly, reaching its peak in about 15-45 minutes, levels off, and finally drops slowly until the polymerization is essentially complete. Stirring and passage of inert gas is continued throughout the entire reaction period.

FIGURE 2

REDOX EMULSION POLYMERIZATION



A	3-Neck Round Bottom Flask
B	Gas Inlet Tube
C	Thermometer
D	Stirring Rod and Bearing
E	Stirring Paddle
F	Addition Funnel
G	Reflux Condenser
H	Adapter
I	Adapter

e. If the polymerization is not completed at this point, add another charge of the secondary initiator and/or warm on a heating bath.

f. Allow the reaction mixture to cool to about 45°C. and then cool rapidly with stirring to room temperature. Strain as indicated above.

C. MULTISTAGE REDOX PROCESS

The single stage redox process can be applied safely to the preparation of polymer emulsions with solids contents of 25-35%. If a higher solids content is desired, a two-stage, or even multiple stage, addition of the ingredients must be resorted to. For a two-stage process, about 80 per cent of the total water charge and about half of the other materials are first converted as above. When the reaction has ceased, the mixture is cooled to the starting temperature and the remaining ingredients are added in the same order and manner as before. The second reaction is then allowed to proceed to completion.

D. REFLUX EMULSION POLYMERIZATION RECIPES

1. POLYMERIZATION OF ETHYL ACRYLATE

Materials

1000	ml.	Deionized Water
96	g.	TRITON X-200
800	g.	Ethyl Acrylate (15 ppm MEHQ)
1.6	g.	Ammonium Persulfate

Procedure

In a 64-oz. (2-qt.) bottle, prepare an emulsion by adding the above ingredients in the given order, holding out 200 ml. of water. This amount of water and 200 ml. of the monomer emulsion are placed in a 3-l. flask fitted as described above. The reaction mixture is stirred and heated in a water bath maintained at 92°C. until the internal temperature reaches 82°C. Refluxing begins at this temperature, indicating a vigorous polymerization, and the temperature rises to 90°C. in 8 minutes. When refluxing subsides, the remaining monomer emulsion is added slowly in 1.5 hours; the reaction mixture is heated to maintain reflux and the internal temperature holds at 88-94°C. After the addition is finished, the temperature is raised to 97°C. to complete the conversion of monomer. The product is then cooled to room temperature with stirring and strained through cheesecloth. An emulsion prepared in this way had the following properties:

Solids Content, % (calculated)	43.4
(found)	42.6
pH at 26°C.	2.9
Viscosity (Brookfield), cps	15.0
Particle Size (light scattering), %[a]	17.4
Minimum Filmforming Temperature, °C.	5

[a] These values represent a relative measurement of particle size in which increasing percentage signifies increasing particle size.

2. COPOLYMERIZATION OF ETHYL ACRYLATE AND METHYL METHACRYLATE

The same procedure applied to a mixture of 400 g. of ethyl acrylate and 400 g. of methyl methacrylate gave a 50/50 emulsion copolymer having the following properties:

Solids Content, % (calculated)	43.4
(found)	43.6
pH at 26°C.	2.7
Viscosity (Brookfield), cps	12.2
Particle Size (light scattering), %[a]	36.0
Minimum Filmforming Temperature, °C.	21
Tukon Film Hardness, KHN units	6.25

3. COPOLYMERIZATION OF ETHYL ACRYLATE, METHYL METHACRYLATE, AND METHACRYLIC ACID

The same procedure formed a terpolymer by using 320 g. of methyl methacrylate (10 ppm MEHQ), 480 g. of ethyl acrylate (15 ppm MEHQ), and 8 g. of glacial methacrylic acid (100 ppm MEHQ). The product had the following properties:

Solids Content, % (calculated)	43.1
(found)	42.9
pH at 26°C.	2.7
Viscosity (Brookfield), cps	11.5
Particle Size (light scattering), %[a]	18.3
Minimum Filmforming Temperature, °C.	9
Tukon Film Hardness, KHN units	1.23

E. REDOX EMULSION POLYMERIZATION RECIPES

1. SINGLE-STAGE PROCESSES

a. POLYMERIZATION OF ETHYL ACRYLATE

Materials

376 ml.	Deionized Water
24 g.	TRITON X-200
200 g.	Ethyl Acrylate (uninhibited)
4 ml.	Ferrous Sulfate Solution: freshly prepared from 0.3 g. $FeSO_4 \cdot 7H_2O$ in 200 ml. deionized water
1 g.	Ammonium Persulfate
1 g.	Sodium Metabisulfite
5 drops	t-Butyl Hydroperoxide (70%)

---

[a] See footnote on page 7.

Procedure

A solution of the emulsifier is prepared in a 1-l. flask, nitrogen flow is started, and the monomer, ferrous solution, and ammonium persulfate are added. After stirring for 15-30 minutes the reaction mixture is cooled to 20°C. and the bisulfite and hydroperoxide are added. The polymerization begins immediately and the temperature rises to 89°C. in one minute, then begins to drop. After 15 minutes, the polymerization is considered to be complete. The product is stirred and cooled to room temperature and strained through cheesecloth.

When an inhibited grade of monomer is used (200 ppm MEHQ), the induction period is about 8 minutes, but the reaction goes at the same rate. The properties of the two emulsions are given below:

	Uninhibited Monomer	Inhibited Monomer
Solids Content, % (calculated)	34.3	34.3
(found)	33.4	33.7
pH at 26-28°C.	2.4	2.5
Viscosity (Brookfield), cps	6.8	6.0
Particle Size (light scattering), %[a]	10.0	13.9
Minimum Filmforming Temperature, °C.	-	12
Tukon Film Hardness, KHN units	-	0.27

b. POLYMERIZATION OF METHYL METHACRYLATE

Methyl methacrylate (10 ppm MEHQ or 50 ppm MEHQ) can be substituted for ethyl acrylate in the above procedure. After an induction period of less than 3 minutes, the temperature rises to 68.5°C. in 11 minutes. An emulsion thus prepared had the following properties:

Solids Content, % (calculated)	34.3
(found)	34.5
pH at 26-28°C.	2.5
Viscosity (Brookfield), cps	6.2
Particle Size (light scattering), %[a]	10.9
Tukon Film Hardness, KHN units	4.93

c. COPOLYMERIZATION OF ETHYL ACRYLATE AND METHYL METHACRYLATE

A mixture of 100 g. of ethyl acrylate (15 ppm MEHQ) and 100 g. of methyl methacrylate (10 ppm MEHQ) is used as before. There is practically no induction period and the peak temperature of 79°C. is reached in 11 minutes. A typical run gave the following emulsion properties:

Solids Content, % (calculated)	34.3
(found)	34.2
pH at 26-28°C.	2.6
Viscosity (Brookfield), cps	6.3
Particle Size (light scattering), %[a]	9.2

[a] See footnote on page 7.

d. COPOLYMERIZATION OF ETHYL ACRYLATE, METHYL METHACRYLATE, AND METHACRYLIC ACID

The procedure of recipe a. is applied to a mixture of 120 g. of ethyl acrylate (15 ppm MEHQ), 80 g. of methyl methacrylate (10 ppm MEHQ), 2 g. of glacial methacrylic acid (100 ppm MEHQ), and 2 g. of ammonium persulfate. Sodium bisulfite is used instead of metabisulfite and is dissolved in 10 ml. of water. t-Butyl hydroperoxide is added in two portions, at the start of the polymerization and at the peak temperature. The induction period is 6 minutes and the maximum temperature 81°C. after 12 minutes. The properties of such a latex were:

Solids Content, % (calculated)	33.3
(found)	33.0
pH at 26-28°C.	2.3
Viscosity (Brookfield), cps	5
Minimum Filmforming Temperature, °C.	5
Tukon Film Hardness, KHN units	1.77

e. COPOLYMERIZATION OF ETHYL ACRYLATE, METHYL METHACRYLATE, AND METHACRYLIC ACID

The reaction mixture of recipe e. is altered by substituting 0.7 g. of sodium formaldehyde sulfoxylate (FORMOPON) for the bisulfite reducing agent and decreasing the amount of ammonium persulfate to 1 g. There is an induction period of 5 minutes and a peak temperature of 89°C. within 2-3 minutes. A latex made in this manner had the following properties:

Solids Content, % (calculated)	34.3
(found)	34.3
pH at 26-28°C.	2.6
Viscosity (Brookfield), cps	6
Minimum Filmforming Temperature, °C.	5
Tukon Film Hardness, KHN units	1.99

f. COPOLYMERIZATION OF METHYL METHACRYLATE, BUTYL ACRYLATE, HYDROXYETHYL METHACRYLATE, AND ACRYLIC ACID

Materials

376	g.	Deionized water
24	g.	TRITON X-200
90	g.	Methyl Methacrylate (10 ppm MEHQ)

---

[a] See footnote on page 7.

90	g.	Butyl Acrylate (5 ppm MEHQ)
20	g.	Hydroxyethyl Methacrylate (HEMA-96%) (200 ppm HQ)
2	g.	Glacial Acrylic Acid (200 ppm MEHQ)
20	ml.	Ferrous Sulfate Solution (0.15%)
1	g.	Ammonium Persulfate in 5 ml. of water
0.7	g.	FORMOPON in 5 ml. of water
7	drops	t-Butyl Hydroperoxide (70%)

After a brief induction period, the temperature rises from 20°C. to 67°C. in about 10 minutes. Cool after stirring 15 minutes and filter through cheesecloth. The amount of gum is negligible and the solids content is 33.1% (calculated 33.9%).

g. COPOLYMERIZATION OF ETHYL ACRYLATE, METHYL METHACRYLATE, AND METHACRYLIC ACID WITH SURFACTANT QS-44 OR SURFACTANT QS-10 AS EMULSIFIER

Materials

375	g.	Deionized Water
5.1	g.	Surfactant QS-44
100	g.	Ethyl Acrylate (15 ppm MEHQ)
100	g.	Methyl Methacrylate (25 ppm MEHQ)
4	g.	Glacial Methacrylic Acid (100 ppm MEHQ)
4	ml.	Ferrous Sulfate Solution (0.15%)
1	g.	Ammonium Persulfate in 5 ml. of water
0.7	g.	FORMOPON in 5 ml. of water
5	drops	t-Butyl Hydroperoxide (70%)

Procedure

In a beaker, stir the surfactant with the water until dissolved and adjust the pH to 9.0 by adding 50% sodium hydroxide solution. Transfer this solution into the reaction flask, rinse the beaker with a small amount of deionized water, add the monomers and ferrous sulfate, and stir 15 minutes with flow of nitrogen before adding the initiators. The maximum temperature of 77°C. is attained in 12-15 minutes. Stir 15 minutes after adding the initiators, then cool to room temperature, adjust to pH 9.5 with 28% aqueous ammonia, and filter; the gums amounted to 0.17%.

The free acid (unneutrallized) surfactant can also be used as an emulsifier for the above copolymerization. In this case, the period of purging with nitrogen after charging the monomers should not exceed 15 minutes before the addition of initiators to avoid the formation of polymer emulsion product with excessive viscosity. Filtration of the finished emulsion gave only 0.05% gums. The properties of these emulsions were:

Surfactant Form	Sodium Salt	Free Acid
Solids Content, % (calculated)	35.0	36.0
(found)	34.3	35.6
pH at 25°C.	5.6	1.8
Viscosity (Brookfield), cps	7.9[a]	10.5[a]
Particle Size (light scattering), %	22.8[b]	12.3[c]
Minimum Filmforming Temperature, °C.	22[a]	30[a]

Surfactant QS-10 can be used instead of Surfactant QS-44 in the same way; 4.1 g. of this emulsifier are dissolved and neutralized before placing in the reaction flask. The peak temperature of 72°C. is obtained in 11 minutes; the finished emulsion was filtered, giving 0.16% gums. The properties of this emulsion were:

Solids Content, % (calculated)	34.9
(found)	34.1
pH at 25°C.	3.6
Viscosity (Brookfield) at pH 9.5, cps	8.7
Particle Size (light scattering), %[d]	11.0

h. COPOLYMERIZATION OF METHYL METHACRYLATE, BUTYL ACRYLATE, HYDROXYETHYL METHACRYLATE (HEMA-30%)[e], AND ACRYLIC ACID USING SURFACTANT QS-44 AS EMULSIFIER

375	g.	Deionized Water
8.4	g.	Surfactant QS-44
100	g.	Hydroxyethyl Methacrylate - 30% (HEMA-30%)
84	g.	Methyl Methacrylate (25 ppm HQ or 10 ppm MEHQ)
84	g.	Butyl Acrylate (5 or 50 ppm MEHQ)
2	g.	Glacial Acrylic Acid (200 ppm MEHQ)
4	g.	Ferrous Sulfate Solution (0.15%)
1	g.	Ammonium Persulfate in 5 ml. of Water
0.35	g.	Sodium Formaldehyde Sulfoxylate (FORMOPON)
5	drops	t-Butyl Hydroperoxide (70%)

---

[a] Emulsion adjusted to pH 9.5 before measurement.

[b] Measurement at 2% solids.

[c] Measurement at 0.4% solids

[d] See footnote on page 7.

[e] HEMA-30% is a solution grade of hydroxyethyl methacrylate containing 30% HEMA and about 3% methacrylic acid in xylene.

Charge the water and Surfactant QS-44 into a 1-l. 3-neck round bottom flask fitted with a stirrer (350 rpm), thermometer, reflux condenser, and gas inlet tube for admitting nitrogen. Mix well under nitrogen, then add the mixture of monomers, cool to 20°C., and stir for 20 minutes. Add the components of the redox initiating system in the stated order. The peak temperature of 54°C. is reached in about 33 minutes. Stir 30 minutes longer, cool to room temperature in an ice bath, and adjust the pH to about 9.0 by careful addition of 9 ml. of 28% aqueous ammonia. Replace the reflux-condenser with a 8-inch air-cooled Vigreux column, short distillation head, 12-inch water cooled condenser, and a vacuum receiver. Warm in a hot water bath to 46°C. internal temperature and carefully reduce the pressure to 75 mm. with a water aspirator. Deionized water is added in 10-ml. portions from an addition funnel to make up for water removed in the stripping; in a typical run, 132 g. of make-up water was required. Under these conditions, the xylene is entirely removed in about 3 hours; the rate of removal of xylene is shown in the following table:

RATE OF REMOVAL OF XYLENE/WATER MIXTURE

Time, minutes	Volume of Xylene ml.	Volume of Xylene cumulative %	Volume of Water ml.
20	19.5	29.5	9
40	35	53.5	20
60	48	73.0	28
80	55	83.0	42
110	59	90.0	59
200	66	100.0	110
220	66	100.0	132

The stripped emulsion is cooled to room temperature and strained through cheesecloth; the amount of gums is negligible.

Solids Content, % (calculated)	34.4
(found)	33.7
Viscosity (Brookfield) at 25°C., cps	12.0
Particle Size (% light scattering)[a]	89.3
pH, before neutralization	1.8
after neutralization	8.9

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[a] See footnote on page 7.

2. TWO-STAGE PROCESSES

a. POLYMERIZATION OF ETHYL ACRYLATE

Materials

First Stage

752	ml.	Deionized Water
48	g.	TRITON X-200
400	g.	Ethyl Acrylate (15 ppm MEHQ)
8	ml.	Ferrous Sulfate Solution (as above)
2	g.	Ammonium Persulfate
2	g.	Sodium Metabisulfite
10	drops	t-Butyl Hydroperoxide (70%)

Second Stage

173	g.	Deionized Water
48	g.	TRITON X-200
400	g.	Ethyl Acrylate (15 ppm MEHQ)
8	ml.	Ferrous Sulfate Solution
2	g.	Ammonium Persulfate in 10 ml. of deionized water
2	g.	Sodium Metabisulfite in 10 ml. of deionized water
10	drops	t-Butyl Hydroperoxide (70%)

Procedure

The first stage is run like recipe E.1.a. to give an induction period of 7 minutes and a temperature peak of 88°C. in 1-2 minutes. After 15 minutes, the temperature falls to 77°C. The reaction mixture is cooled to 20°C. with stirring and the ingredients of the second stage are added in the stated order. An induction period of 1.5-5.5 minutes and a maximum temperature of 70.5°C. after 2 minutes are observed. The temperature remains at 70°C. for five minutes before beginning to fall. The properties of such an emulsion were:

Solids Content, % (calculated)	43.2
(found)	42.7
pH at 26-28°C.	2.2
Viscosity (Brookfield), cps	16.2
Particle Size (light scattering), %[a]	13.2
Minimum Filmforming Temperature, °C.	9
Tukon Film Hardness, KHN units	1.0

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[a] See footnote on page 7.

b. COPOLYMERIZATION OF ETHYL ACRYLATE, METHYL METHACRYLATE, AND METHACRYLIC ACID USING TRITON X-305 AS EMULSIFIER

Materials

First Stage

1000	ml.	Deionized Water
31.6	g.	TRITON X-305
253	g.	Ethyl Acrylate (15 ppm MEHQ)
168	g.	Methyl Methacrylate (10 ppm MEHQ)
4	g.	Glacial Methacrylic Acid (100 ppm MEHQ)
0.5	g.	Ammonium Persulfate
0.6	g.	Sodium Hydrosulfite (LYKOPON) in 6 ml. of water

Second Stage

35	g.	TRITON X-305
283	g.	Ethyl Acrylate (15 ppm MEHQ)
188	g.	Methyl Methacrylate (10 ppm MEHQ)
5	g.	Glacial Methacrylic Acid (100 ppm MEHQ)
0.6	g.	Ammonium Persulfate in 1.5 ml. of water
0.8	g.	LYKOPON in 6 ml. of water

Procedure

The first stage reaction mixture is cooled to 15°C. before adding the initiator and reducing agent. The peak temperature of 65°C. is reached in about 30 minutes. After 5 minutes, the reactants are stirred and cooled to 15°C. and the second stage ingredients are added in the stated order; the methacrylic acid should be dissolved in one of the other monomers. A peak of 65°C. is again attained and the mixture is stirred for 60 minutes before cooling to 30°C. The pH is then adjusted to 9.5 by adding 28% aqueous ammonia and the product is strained as before. The solids content is close to the calculated level of 46%.

c. COPOLYMERIZATION OF ETHYL ACRYLATE, METHYL METHACRYLATE, AND ACRYLIC ACID USING TRITON X-405 AS EMULSIFIER

Materials

First Stage

1000	ml.	Deionized Water
30	g.	TRITON X-405
260	g.	Ethyl Acrylate (15 ppm MEHQ)
155	g.	Methyl Methacrylate (10 ppm MEHQ)

4	g.	Glacial Acrylic Acid (250 ppm MEHQ) in 56 g. of deionized water
0.6	g.	Ammonium Persulfate in 1.5 ml. of water
0.7	g.	Sodium Hydrosulfite (LYKOPON) in 6 ml. of water.

Second Stage

30	g.	TRITON X-405
300	g.	Ethyl Acrylate (15 ppm MEHQ)
175	g.	Methyl Methacrylate (10 ppm MEHQ)
5	g.	Glacial Acrylic Acid (250 ppm MEHQ) in 65 ml. of deionized water
0.6	g.	Ammonium Persulfate in 1.5 ml. of water
0.8	g.	LYKOPON in 6 ml. of water

Procedure

The reactants and catalyst system are combined at 20°C. but the acrylic acid solution is added while the temperature rises to 60°C. After stirring at 60°C. for 1 hour, the emulsion is cooled to 20°C., the second stage materials are added, and the reaction mixture is stirred at 70°C. for 60 minutes after the peak has been reached. The product is then cooled to 20°C. and neutralized to pH 9.5 with 28% aqueous ammonia before straining. The solids content is about 45.0% (calculated 45.5%).

d. COPOLYMERIZATION OF ETHYL ACRYLATE, METHYL METHACRYLATE, AND METHACRYLIC ACID USING TRITON X-301 AS EMULSIFIER

Materials

First Stage

380	g.	Deionized Water
29	g.	TRITON X-301
126	g.	Ethyl Acrylate (15 ppm MEHQ)
63	g.	Methyl Methacrylate (10 ppm MEHQ)
4	g.	Glacial Methacrylic Acid (100 ppm MEHQ)
2	ml.	Ferrous Sulfate Solution (0.15%)
0.4	g.	Ammonium Persulfate
0.4	g.	LYKOPON

Second Stage

39	g.	Deionized Water
33	g.	TRITON X-301
144	g.	Ethyl Acrylate (15 ppm MEHQ)
72	g.	Methyl Methacrylate (10 ppm MEHQ)
4.5	g.	Glacial Methacrylic Acid (100 ppm MEHQ)
2	ml.	Ferrous Sulfate Solution (0.15%)
0.5	g.	Ammonium Persulfate in 10 ml. of water
0.5	g.	LYKOPON in 10 ml. of water
5	drops	t-Butyl Hydroperoxide (70%)

Procedure

The initiating system in the first stage is added at 20°C. The induction period is 3-5 minutes and the maximum temperature of 84°C. is reached in about 20 minutes. After cooling below 30°C., the second stage ingredients are added in order, dissolving the methacrylic acid in one of the other monomers and the redox ingredients in water before addition. The temperature rises to 73°C. in 15 to 20 minutes. The hydroperoxide is then added to assist in completing the polymerization. The emulsion is then heated in a water bath at 65-73°C. for 1 hour. The product is finally cooled to 30°C., the pH is adjusted to 9.5 by adding about 10 ml. of 28% aqueous ammonia, and the whole is stirred 15 minutes before straining. The solids content of the finished polymer emulsion is about 45%.

e. COPOLYMERIZATION OF ETHYL ACRYLATE, METHYL METHACRYLATE, AND METHACRYLIC ACID WITH SURFACTANT QS-44 OR SURFACTANT QS-10 AS EMULSIFIER

First Stage

A single-stage polymer emulsion is prepared by the procedure of recipe E.1.h. and cooled to 20-25°C.

Second Stage

Materials

90	g.	Deionized Water
5.1	g.	Surfactant QS-44
100	g.	Ethyl Acrylate (15 ppm MEHQ)
100	g.	Methyl Methacrylate (10 ppm MEHQ)

4	g.	Glacial Methacrylic Acid (100 ppm MEHQ)
4	g.	Ferrous Sulfate Solution (0.15%)
1	g.	Ammonium Persulfate in 5 ml. of water
0.7	g.	FORMOPON in 5 ml. of water
5 drops		t-Butyl Hydroperoxide (70%)

The emulsifier is dissolved and neutralized as before, the monomers are added and shaken with the surfactant solution to form an emulsion, which is then charged to the reaction flask. Stir 15 minutes while passing in nitrogen, cool to 20°C., and add the redox system. A peak of 65°C. is reached in 7-10 minutes. Continue stirring for 15 minutes, cool, and adjust the pH to 9.5 if desired before straining.

The emulsifier may be neutralized with potassium hydroxide with similar results. Surfactant QS-10 may be substituted using 4.1 g. of the material as supplied (100% solids). The properties of these emulsions are given below. The buffering action of Surfactant QS-44 and Surfactant QS-10 may be seen by comparing the pH of these emulsions with the pH of a product made with TRITON X-200 (recipe 2a., page 14).

	SURFACTANT QS-44	SURFACTANT QS-10
Solids Content, % (calculated)	45.9	46.0
(found)	45.4	45.9
pH at 25°C.	5.8	6.35
Viscosity (Brookfield), cps at pH 9.5	35.5	35.7
Particle Size (light scattering), %[a]	23.6	46.7

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[a] See footnote on page 7.

CHAPTER III

FUNDAMENTALS OF EMULSION POLYMERIZATION

The emulsion polymerization process is very complex for it involves seldom less than four ingredients and often more as well as variations in reaction conditions. Most knowledge of the process is empirical although theoretical understanding is slowly improving. Because the purpose of this bulletin is practical, only a qualitative picture of the present theory of the process and of related phenomena, such as the general properties of emulsions and of initiator systems, is given here. Those seeking discussions of the quantitative aspects of the process should consult the reviews of Gerrens (III-1) and van der Hoff (III-2). Many monographs on the properties of aqueous solutions of surfactants and of emulsions are available; among these, the monograph by Becher (III-3) is typical.

A. EMULSIONS AND THEIR PROPERTIES

An emulsion is a two phase system containing two liquids that are mutually insoluble or sparingly soluble under normal conditions and to which an emulsifier is added. In oil-in-water emulsions, which are the concern of this bulletin, the external phase is water containing salts, buffers, initiators, and saturated with emulsifier. The internal oil phase may be swollen micelles of the emulsifier and monomer droplets at the start of a polymerization reaction or, in the final product, polymer particles on whose surfaces the emulsifier is adsorbed. If no emulsifier is present, emulsions of brief durability can be produced by vigorous agitation. The addition of a suitable surfactant in amounts above a critical concentration permits the dispersion of the stirred monomer phase into a stable system. At somewhat higher concentration of the emulsifier, flocculation of the polymer particles during or after the reaction is prevented unless the composition or energy of the system are greatly changed. Deemulsification can thus be brought about by adding electrolytes or water-miscible solvents, by evaporation or freezing, or by severe mechanical stress.

Surfactants, among which emulsifiers are a special class, are substances having limited solubility in water but are capable of forming hydrated aggregates called micelles when the critical micelle concentration (c.m.c.) is exceeded. These aggregates often comprise 50 to 100 molecules of surfactant and are capable of imbibing water and monomers. Micelles can form because surfactant molecules are composed of mutually repellent polar or ionic portions and nonpolar or nonionic portions. In these aggregates, the hydrophilic polar or ionic portions are oriented toward the external aqueous phase while the hydrophobic nonpolar or nonionic portions are oriented inwardly. The whole system is stabilized at the interface between the water and micelles by a double electrical layer or by an associated atmosphere of water molecules. When a monomer (or other water-insoluble liquid) is present, the micelles are somewhat swelled by imbibing monomer, thus increasing the solubility of the latter. The extent of solubilization depends on the monomer and the emulsifier; speaking relatively, the increase is usually greater for the less soluble monomers. If the monomer concentration exceeds this enhanced solubility, the remainder can be broken up by stirring to form emulsified droplets partially stabilized by the adsorption of some emulsifier on their surfaces. The relative number and size of the micelles and monomer droplets are important. In the usual recipe, like those given in Chapter II, there are about 10^{10}-10^{11} monomer droplets per milliliter of water having diameters of about 1μ (10,000Å) or more and about 10^{18} micelles per milliliter with diameters of 50-100Å. It will be shown in the next section that the diameter of the polymer particles is dependent on the concentrations of the emulsifier and initiator.

B. EMULSION POLYMERIZATION

The fourth ingredient of a polymerization mixture, which differentiates such mixtures from ordinary emulsions, is the initiator, a substance or combination of substances capable of supplying free radicals. In acrylic emulsion polymerizations, water-soluble peroxidic salts, such as ammonium or potassium persulfate, are normally used as initiators; sometimes small amounts of peroxides may also be added. The initiating particles result from the dissociation of the persulfate anion at sufficiently high temperatures into sulfate radical anions (III-4).

$$^{-}O_3S\text{-}O\text{-}O\text{-}SO_3^{-} \longrightarrow {}_2SO_4^{\cdot -}$$

The rate of dissociation increases with rising temperature or in the presence of activating polyvalent ions and/or reducing agents. At the concentrations of persulfates normally employed, about 10^{13} radicals per milliliter of water per second are formed at 50°C. A large proportion of these primary radicals are effective in initiating polymerization which begins by attack of the sulfate radical anions on those molecules of monomer (M) dissolved in the aqueous phase to form new ion radicals:

$$SO_4^{\cdot -} + M \longrightarrow SO_4M\cdot$$

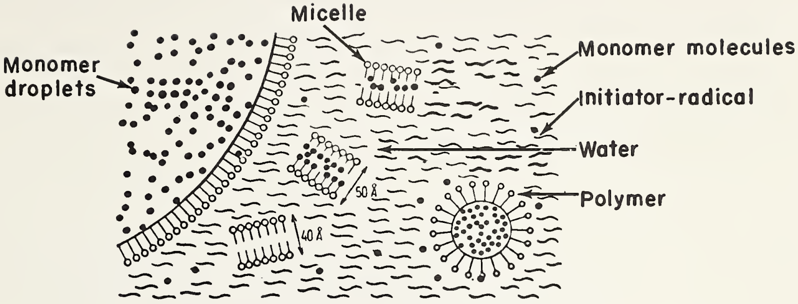
Initiation

$$^{-}SO_4M\cdot + xM \longrightarrow {}^{-}SO_4(M)_xM\cdot$$

Propagation

The chains begin growing by addition of more molecules of monomer to the radicals in the aqueous phase. The polymer-containing radicals soon enter the micelles where propagation of the chain is continued by attack on the solubilized monomer. The radicals enter the micelles rather than the monomer droplets because, as shown above, the number of micelles is enormously greater. The radicals may also be viewed as surfactant-like bodies having ionic and nonionic portions, and since they are capable of participating in the dynamic equilibrium between the micellar and dissolved emulsifier, their movement into the micelles is favored. Growth of the polymer chains within the micelles is very fast and is supported by rapid diffusion of monomer from the droplets into the growing micelles. As a result of such growth, the micelles expand tremendously and the polymer particles eventually attain a diameter of 0.1-1μ (1000-10,000Å). The situation existing in the reaction mixture is sketched in Figure 3.

FIGURE 3



Schematic Representation of an Emulsion Polymerization
H. Gerrens, Ber. Bunsenges. Physik. Chem. **67**, 741 (1963).
Courtesy of Verlag Chemie G.m.b.H.

The propagation process is terminated when a second radical enters the micelle where growth is occurring and combines more or less rapidly with the original radical chain:

$$^{-}SO_4(M)_yM\cdot \; + \; ^{-}SO_4(M)_xM\cdot \longrightarrow \; ^{-}SO_4(M)_{x+y}SO_4^{-}$$

Termination (by combination)

Although the termination reaction given in the equation involves combination, some polymer radicals may be terminated by disproportionation:

$$^{-}SO_4(M)_yM\cdot \; + \; ^{-}SO_4(M)_xM\cdot \longrightarrow \; ^{-}SO_4(M)_yMH \; + \; ^{-}SO_4(M)_{x+1}$$

Termination (by disproportionation)

The invasion of the second radical is infrequent compared to the propagation rates of acrylic monomers; the chains thus have an opportunity to become very long. In the case of acrylic emulsion polymers, the molecular weights, therefore, are often well above 1×10^6. Under some circumstances, especially in large viscous polymer-monomer particles, the second entering radical cannot come into contact with the existing growing radical in the particle and therefore begins the propagation of a second chain. Initiating radicals continue to enter the particles from time to time to start new chains or to terminate old ones until the monomer is completely exhausted.

As the micelles expand, molecules of dissolved surfactant are adsorbed on the surfaces of the growing polymer particles. The micellar surfactant gradually goes into solution and is then adsorbed, so that micelles disappear altogether at about 10-20% conversion of monomer. At the end of the process, all but a small proportion of emulsifier is adsorbed on the polymer particles. The diffusion of monomers from the droplets into the growing particles continues until the droplets are also consumed; in the case of methyl methacrylate, this occurs at about 30% conversion. From this point on, the rate of polymerization, which is relatively constant during the early stages, would be expected to fall off. In most acrylic polymerizations, however, this does not happen until much later because of the gel or Trommsdorff effect and the reaction therefore proceeds rapidly to a virtually quantitative conversion. The final number of particles, which remains substantially unchanged after the disappearance of the micelles, is considerably smaller than the number of micelles because the latter have disintegrated after only a small proportion (about 1 in 700-1000) has furnished reaction sites. In the final emulsion product, the usual concentration of polymer particles having diameters of 0.1-1μ is about 10^{13} to 10^{15} per milliliter of water.

The quantitative aspects of the above picture of the emulsion polymerization process were first worked out by Smith and Ewart (III-5) and were modified later by others (III-6,7) to account for departures from "ideal behavior" . These theories have been extended and reviewed recently (III-1,2). In addition there are specific reports on the polymerization of methyl and butyl methacrylates (III-8,9,10). These papers should be consulted for their discussions of the details of emulsion processes. Here we can only call attention to the principal equations of the Smith-Ewart theory. The overall rate of polymerization R_p is described in terms of the number of particles per liter of organic phase N, the propagation rate constant k_p, the concentration of monomer [M], and Avogadro's number, $N_A = 6.06 \times 10^{23}$:

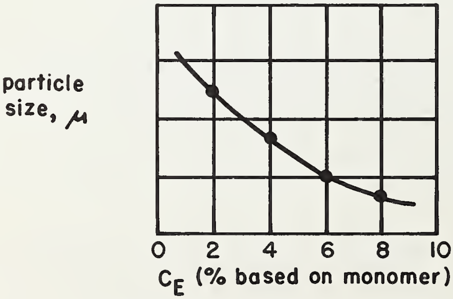
$$R_p = Nk_p[M]/2N_A$$

This equation shows that the rate of polymerization is directly dependent on the number of particles which is in turn proportional to the concentration of emulsifier, C_E, and initiator, C_I, by the following exponential relationship:

$$N \propto C_E^{0.6} \times C_I^{0.4}$$

Since the particle size is inversely proportional to the number of particles, the particle size at constant initiator concentration drops exponentially with increasing concentration of emulsifier and approaches a minimum value at about 8% of emulsifier (based on monomer). This relation is shown in general terms in Figure 4. The exact shape of the curve will be influenced by the polymer and the nature of the emulsifier.

FIGURE 4



A similar curve could be obtained for the relation of particle size to initiator concentration. From a practical standpoint, however, the principal influence on the particle size is the concentration of emulsifier because the initiator concentration is not varied over a very wide range.

C. INITIATING SYSTEMS

As indicated above, persulfate salts are the principal initiators used in acrylic emulsion polymerization processes. Thermolytic cleavage at the peroxy linkages of persulfate anions forms sulfate radical anions which act as the primary initiators:

$$^{-}O_3S\text{-}O\text{-}O\text{-}SO_3^{-} \longrightarrow 2SO_4^{\dot{-}}$$

The rate of dissociation and hence the concentration of radicals increase with temperature and with concentration of persulfate by a first order law at constant temperature (Table III-1). From the rate constants at 50-90°C., the energy of activation for the dissociation has been calculated to be 33.5 kcal/mole (III-11).

TABLE III-1

Radical Concentrations in 0.01M Potassium Persulfate Solution (pH 10) (III-12)

Temperature, °C.	Radicals/ml. sec.
50	8.4×10^{12}
70	1.7×10^{14}
90	2.5×10^{15}

Although induced and secondary decomposition reactions can occur, these are largely suppressed in the presence of a polymerizable monomer (III-13).

The rate of dissociation of persulfates at a given temperature can be greatly accelerated by the addition of certain reducing agents and/or small amounts of certain salts of polyvalent metals that act as activators. In addition to increased radical concentration, these compound systems (redox systems) also exhibit greatly reduced inhibition periods as compared to the persulfates themselves. The principal reducing agent components of redox systems are salts of the lower oxyacids of sulfur such as sodium bisulfite ($NaHSO_3$) or metabisulfite ($Na_2S_2O_5$), sodium hydrosulfite ($Na_2S_2O_4$, LYKOPON)[a], sodium thiosulfate ($Na_2S_2O_3$), and sodium formaldehyde sulfoxylate ($NaHSO_2 \cdot CH_2O \cdot 2H_2O$, FORMOPON)[a]. Iron salts such as ferrous sulfate ($FeSO_4 \cdot 7H_2O$) or ferrous ammonium sulfate ($Fe[NH_4]_2[SO_4]_2 \cdot 6H_2O$) are the most commonly used activators. When all three components of a redox system are present, the energy of activation for the dissociation of persulfate anions is lowered from 33.5 kcal/mole to about 12 kcal/mole (III-14); it is this large reduction in energy requirements that facilitates the formation of radicals in redox initiation.

There are indications of differences between the actual initiators involved in reflux (thermally activated) and redox (chemically activated) systems. Information on the nature of the actual initiating species can be obtained by analyses of the end groups on the polymer products. Tracer (III-15) and chemical (III-4) methods have indicated the presence of sulfate end groups, as would be expected from the formation of such radicals by the dissociation of persulfate. Colorimetric studies of polymers produced by reflux processes with persulfate alone have found both sulfate and hydroxyl end groups; the presence of hydroxyl groups suggests that a secondary reaction between the sulfate radicals and water can produce hydroxyl radicals, also capable of initiating the polymerization (III-16, 17):

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[a] FORMOPON and LYKOPON are supplied by the Special Products Department. Information on their properties and applications is available in Bulletin SP-21.

$$SO_4^{\dot{-}} + H_2O \longrightarrow HSO_4^{=} + HO\cdot$$

The persulfate and reducing agent components of redox initiators provide sulfate and sulfonate end groups, respectively (III-18). It is possible that the nature of the end groups may exert some influence on the stability, water sensitivity, and corrosivity of polymer emulsions.

Although the reactions in a three-component initiator system are complex, the following are probably the most important and illustrate the possibilities; thiosulfate is an example of a typical reducing agent:

$$S_2O_8^{=} + Fe^{++} \longrightarrow SO_4^{\dot{-}} + SO_4^{=} + Fe^{+++} \tag{1}$$

$$S_2O_8^{=} + 2S_2O_3^{=} \longrightarrow S_4O_6^{=} + 2SO_4^{\dot{-}} \tag{2}$$

$$Fe^{+++} + 2S_2O_3^{=} \longrightarrow Fe^{++} + S_4O_6^{=} \tag{3}$$

Equations (2) and (3) can be replaced by similar equations for FORMOPON (III-19):

$$S_2O_8^{=} + HOCH_2SO_2^{-} + OH^{-} \longrightarrow 2SO_3^{\dot{-}}(HCHO) + SO_4^{=} + H_2O \tag{4}$$

$$Fe^{+++} + HOCH_2SO_2^{-} + OH^{-} \longrightarrow Fe^{++} + SO_2^{\dot{-}}(HCHO) + SO_4^{=} + H_2O \tag{5}$$

The rate of radical formation is most sensitive to the concentration of ferrous ion, less dependent on the reducing agent, and still less so on persulfate. This suggests that the rate-determining step is the reduction of ferric to ferrous ion (equations 3 or 5). The fact that brief periods of initiation occur with mixtures of ferrous ion and persulfate mixtures supports this hypothesis. Such polymerizations soon come to a halt because of the rapid conversion to ferric ion but can be renewed by adding the reducing agent, thus completing the cycle of ferrous-ferric-ferrous ions whereby a steady and copious supply of primary radicals is formed.

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CHAPTER IV

PROCESS VARIABLES IN EMULSION POLYMERIZATIONS

The principal components of emulsion polymerization recipes, as shown in Chapter II, are monomer(s), water, emulsifiers, and initiators. In some instances buffers, salts, and chain regulators may also be included. The success and efficiency of emulsion processes are dependent on the quality and amounts of these components as well as the temperature, time, addition schedule, and agitation.

A. COMPONENTS

1. ACRYLIC MONOMERS

a. GENERAL PROPERTIES

The Rohm and Haas Company offers 20 acrylic monomers, including alkyl acrylates and methacrylates, functionally substituted methacrylic esters, acrylic and methacrylic acid, and methacrylamide. The physical properties and inhibitor grades of these monomers are listed in Table IV-1. Additional information on these products is given in the following bulletins:

SP-60	Acrylic and Methacrylic Acids and Esters. Typical Properties and Specifications.
SP-130	Storage and Handling of Acrylic and Methacrylic Esters and Acids
SP-256	Low Inhibitor Grades of Acrylic and Methacrylic Esters and Acids
SP-236	Isobutyl Methacrylate (IBMA)
SP-237	1,3-Butylene Dimethacrylate (BDMA)
SP-88	Glacial Methacrylic Acid and Glacial Acrylic Acid
SP-216	2-Hydroxyethyl Methacrylate (HEMA) and Hydroxypropyl Methacrylate (HPMA)
SP-84	t-Butylaminoethyl Methacrylate and Dimethylaminoethyl Methacrylate
SP-32	Methacrylamide
SP-71P	Acrylic Monomers Price Schedule

TABLE IV-1

PHYSICAL PROPERTIES AND INHIBITOR GRADES OF ACRYLIC MONOMERS

Monomer	Density lb/gal	Flash Point Open Cup °F. (a)	Solubility in Water at 25°C. g/100 g	Inhibitor Grades, ppm (b)		
				MEHQ	HQ	BHT
Methyl Acrylate	7.92	50 T	5	15,200,1000		
Ethyl Acrylate	7.65	50 T	1.5	15,200	1000	
Butyl Acrylate	7.46	120 C	0.2	5,50		
2-Ethylhexyl Acrylate	7.35	195 C	0.01	50,100	100	
Acrylic Acid	8.70	155 C	Infinite	200		
Methyl Methacrylate	7.83	55 T	1.5	10,50,100	25,60	35
Ethyl Methacrylate	7.58	70 T	Low	15	100	
Butyl Methacrylate	7.40	150 C	Insoluble	10	100	
Isobutyl Methacrylate	7.35	120 T	Insoluble	10		
Lauryl Methacrylate	7.23	270 C	Insoluble	100		
Stearyl Methacrylate	7.20	>300 C	Insoluble	100		
1,3-Butylene Dimethacrylate	8.42	205 C	Insoluble	100		
Hydroxyethyl Methacrylate (96%)	8.86	227 C	Infinite		200	
Hydroxyethyl Methacrylate (30%)	7.73	80 T	Insoluble	350		
Hydroxypropyl Methacrylate (96%)	8.55	250 C	Limited		200	
Hydroxypropyl Methacrylate (40%)	7.75	90 T	Insoluble	400		
Dimethylaminoethyl Methacrylate	7.77	165 C	Infinite	2000		
t-Butylaminoethyl Methacrylate	7.61	185 C	1.8 (d)	1000		
Methacrylic Acid	8.45	170 C	Infinite	100,250	1000	
Methacrylamide	(c)		37.4/30°C.			

(a) T - Tagliabue Open Cup; C - Cleveland Open Cup

(b) MEHQ - monomethyl ether of hydroquinone; HQ - hydroquinone; BHT - butylated hydroxytoluene

(c) Solid product, uninhibited, m. p. 110°C.

(d) Slowly hydrolyzed in aqueous solution

Rohm and Haas acrylic monomers are available in commercial quantities and supplied in bulk, drums, and small packages. They are chemicals of high purity, most of them having purities of 99% or better. Although uninhibited grades of some monomers are available, inhibited grades are completely satisfactory for direct use in emulsion polymerization processes. Particular attention is called to the following low inhibitor grades of Rohm and Haas acrylic monomers stabilized with the monomethyl ether of hydroquinone (MEHQ) or butylated hydroxytoluene (BHT):

Low Inhibitor Grades of Acrylic Monomers

Methyl Acrylate	15 ppm MEHQ	Methyl Methacrylate	35 ppm BHT
Ethyl Acrylate	15 ppm MEHQ	Ethyl Methacrylate	15 ppm MEHQ
Butyl Acrylate	5 ppm MEHQ	Butyl Methacrylate	10 ppm MEHQ
2-Ethylhexyl Acrylate	50 ppm MEHQ	Isobutyl Methacrylate	10 ppm MEHQ
Methyl Methacrylate	10 ppm MEHQ	Methacrylic Acid	100 ppm MEHQ

These products are the lowest inhibitor grades of acrylic monomers available. Although the older more highly inhibited grades have been and are still successfully used in emulsion polymerization, these low inhibitor grades are preferred for the manufacture of emulsion polymers. In addition, combinations of these grades provide the lowest total inhibitor contents for copolymerization with other monomers. Their utilization offers economic and technical advantages arising from the possibility of shorter processing cycles, decreased induction periods, faster overall reaction rates, smoother and more reproducible polymerizations, more complete conversion of monomers, and superior color. In addition, the minimum amounts of initiators may be used to promote polymerization. The low inhibitor grades of Rohm and Haas acrylic monomers are classified as fully inhibited. Recommendations for storage and handling of these grades are therefore identical with those made for the older more highly inhibited products.

b. POLYMERIZATION PROPERTIES

Acrylic compounds are among the more reactive monomers in polymerization reactions. The polymerization of acrylate esters or acrylic acid is very rapid and is accompanied by the liberation of large amounts of heat. The rates and heats of polymerization for methacrylic derivatives are somewhat lower. Although the overall rates in emulsion processes may be 10 to 100 times faster than in bulk or solution, the initial rates obtained by bulk or solution methods are instructive (Table IV-2). Unfortunately, there are no similar comprehensive data for emulsion homopolymerizations and the complexities of copolymerization kinetics are even less well known. The relative ease of polymerization of acrylic monomers does, however, extend to emulsion processes as may be seen from the short reaction periods of the recipes given in a previous chapter. The heats of polymerization are the same regardless of process.

Some difficulties have been reported for the polymerization of the higher acrylates and methacrylates. As the ester alkyl chain lengthens, solubilization of the monomer by the surfactant becomes increasingly difficult and the rate of polymerization and the yield drop severely. Several remedies have been suggested to overcome this problem. One approach is the use of a mixed emulsifier system comprising both anionic and nonionic surfactants.

TABLE IV-2

PROPERTIES OF ACRYLIC MONOMERS AND POLYMERS

Monomer (M_1)	Heat of Polymerization Kcal/mole	Heat of Polymerization BTU/lb	Specific Heat cal/g/°C. Monomer	Specific Heat cal/g/°C. Polymer	k in Initial Rate of Polymerization 44.1°C., % hr.[b]	Copolymerization Parameters: Reactivity Ratios r_1	Reactivity Ratios r_2(styrene)	Q	e
Methyl Acrylate	18.8	394	0.48		250	0.14	0.68	0.43	0.73
Ethyl Acrylate	18.6	335	0.47		313	0.16	1.01	0.34	0.58
Butyl Acrylate	18.5	261	0.46			0.21	0.82	0.43	0.53
2-Ethylhexyl Acrylate	14.5	142	0.45			0.26	0.94	0.41	0.39
Acrylic Acid	18.5	463	0.50			0.35	0.21	1.09	0.98
Acrylonitrile	17.3	587	0.50			0.04	0.40	0.58	1.13
Methyl Methacrylate	13.8	248	0.45	0.35	27	0.46	0.52	0.74	0.40
Ethyl Methacrylate	13.8	218	0.45		25	0.33	0.55	0.64	0.50
Butyl Methacrylate	14.2	180			41	0.47	0.52	0.74	0.39
Isobutyl Methacrylate	14.3	182				0.58	0.56	0.76	0.26
Lauryl Methacrylate					346	0.57	0.63	0.74	0.20
Hydroxyethyl Methacrylate	11.9	197				0.65^a	0.57^a	0.93	0.4
Hydroxypropyl Methacrylate	12.1	151				0.65	0.56	0.79	0.20
Dimethylaminoethyl Methacrylate					66	0.37	0.53	0.68	0.48
t-Butylaminoethyl Methacrylate					50	0.83	0.47	0.98	0.17
Methacrylic Acid	15.8	331	0.50		71	0.70	0.15	2.37	0.83
Methacrylamide	13.5	295				0.12^a	0.13^a	1.46	1.24
Styrene	16.6	287	0.42	0.32	6			1.0	-0.8
Vinyl Acetate	21.3	446	0.26	0.39		0.01	55	0.026	-0.22
Vinylidene Chloride	14.4	272	0.27	0.32		0.14	2.0	0.19	0.49

a - Calculated from reactivity ratios with methyl methacrylate.

b - Initial rate of polymerization (% 1hr.) = $k\sqrt{[AIBN]}$ (See Bulletin SP-251).

Such a combination has long been known to be effective for butadiene-styrene copolymers (IV-1) and has also been recommended for the copolymerization of vinyl acetate with acrylate esters from butyl to decyl (IV-2) to improve the rate and to avoid the appearance of graininess in the final emulsion. Other examples of the use of mixed emulsifier systems will be cited in the discussion of surfactants.

Another suggested method is the addition of water-soluble organic solvents like acetone or methanol to the aqueous phase (IV-3). Monomers such as lauryl or stearyl methacrylates have a solubility below 1 per cent in mixtures of 85 parts of methanol or acetone and 25 parts of water. They are reported to be readily emulsified with ionic surfactants in aqueous media containing 20-30% of the solvents to give excellent conversions to stable polymer emulsions with particle diameters between 0.6 and 1μ. If desired, the solvent may be removed from the final product by steam distillation.[a]

Functionally substituted acrylic monomers with high water solubility are distributed between the water phase and monomer droplets. Experience has shown that the normal methods of emulsion polymerization can be applied to such systems. Since amino-substituted methacrylates, like dimethylaminoethyl or t-butylaminoethyl methacrylate, and other basic monomers might form insoluble products with anionic surfactants, a combined emulsifier using 4-6% of the nonionic TRITON X-405 and 0.5-1% of sodium lauryl sulfate (based on monomer) has been recommended (IV-4,5). The solution grade of hydroxyethyl methacrylate (HEMA-30%), a xylene solution containing 30% of the monomer and 3% of methacrylic acid, can also be incorporated into copolymers by using Surfactant QS-44 as the emulsifier. At the end of the polymerization, the solvent is steam distilled to give the finished emulsion product; see Chapter II, page 12, recipe E.1.h.

Table IV-2 also lists the monomer reactivity ratios of acrylic monomers (M_1) with styrene (M_2) and the Price-Alfrey copolymerization parameters Q and e. They were determined by the Research Division of the Rohm and Haas Co. The parameters are significant because monomers are not incorporated into copolymers at equal rates. These differences are represented quantitatively as the monomer reactivity ratios which are the same in emulsion as in other processes (IV-6-9). The differences in reactivity cause the first-formed copolymer to contain a higher proportion of the more reactive monomer than is present in the reaction mixture. The last copolymer to be formed is similarly enriched in the less reactive compound and may even be homopolymer in extreme cases. This non-uniformity may or may not be of consequence in affecting the usefulness of a product in a specific application.

If a more homogeneous composition seems desirable, incremental additions of the more reactive monomer can be made during the reaction (IV-10,11). This is illustrated for the addition of acrylic acid in recipe 3c, Chapter II. Recommendations for more sophisticated addition schedules are determined by an electronic computer (IV-12)[b].

In some cases non-uniformity is deliberately sought to achieve a particular balance of properties in the polymer product (IV-10,13-15). This may be accomplished by changing the composition of the monomer mixture while it is being charged during a reflux process or at the successive stages of a multi-stage redox recipe. The composition of the polymer may thus be varied from a slight alteration to complete disparity represented by graft and block copolymers (IV-16).

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[a] Further information on this process for the emulsion polymerization of higher methacrylates is available from Special Products Department.

[b] The Special Products Department can provide programmed addition schedules for reactive monomers in binary mixtures and, under special conditions, in ternary mixtures. Discussion of this and other programs involving the calculation of copolymer composition is invited.

The influence of the differences among the various acrylic monomers in the polymerization process has been pointed out. A broad range of properties can be obtained from the large variety of possible products based on different combinations of acrylic and other monomers. These properties are decisive for the selection of products in applications. A discussion of the relationship of polymer properties to the requirements of applications is beyond the scope of this bulletin. Examples of acrylic emulsion copolymers reported to be useful in certain applications may be found in other bulletins of the Special Products Department (see above) and elsewhere (IV-17).

The effects of various methods used for the addition of monomers are discussed in the section entitled "Surfactants".

2. WATER

a. QUANTITY OF WATER

Water is required as a dispersion medium in emulsification and a heat transfer medium in emulsion polymerization. It is also a solvent for the surfactants and initiators. In reflux processes, the presence of water keeps the overall viscosity of the reaction mixture at a low level and thus allows easy agitation and heat transfer. Redox processes require the use of sufficient water to absorb all of the heat of polymerization. The monomer-water ratio must be low enough to accomplish the dissipation of heat. Emulsions with high solids content must therefore be prepared in several stages as illustrated by the recipes of part 3, Chapter II. The correct charge of monomer and water is determined by calculating the expected rise in temperature from the heat of polymerization and the specific heat of the monomers (or polymer) and water (Table IV-2). Minor constituents, such as initiators and surfactants, may be ignored, but the water associated with them is taken into account. An example of the expected rise in temperature during a two-stage redox process (recipe 3d) is given in Table IV-3. During the second stage, it is assumed that the specific heat of polymer is the same as for poly(methyl methacrylate), since values for other acrylic polymers are not available. Comparison of the calculated increase agrees quite well with the actual observations. The calculated value will usually be found to be somewhat higher than the observed rise.

TABLE IV-3

TEMPERATURE RISE IN ACRYLIC EMULSION POLYMERIZATION

Recipe 3d.	Component	Grams	Heat Capacity, cal/°C.	Heat of Polymerization, cal.
Stage 1	Water	406	406 x 1.0 = 406	
	Ethyl Acrylate	126	126 x 0.47 = 59	$\frac{126}{100} \times 18600 = 23436$
	Methyl Methacrylate	63	63 x 0.45 = 28	$\frac{63}{100} \times 13800 = 8694$
	Methacrylic Acid	4	4 x 0.50 = 2	$\frac{4}{86} \times 15800 = 735$
			495	32865

$$\Delta T = \frac{32865}{495} = 66^\circ C. \quad \text{Found } 64^\circ C.$$

Recipe 3d.	Component	Grams	Heat Capacity, cal/°C.	Heat of Polymerization, cal.
Stage 2	Water	494	494 x 1.0 = 494	
	Polymer	193	193 x 0.35 = 67	
	Ethyl Acrylate	144	144 x 0.47 = 68	$\frac{144}{100} \times 18600 = 26784$
	Methyl Methacrylate	72	72 x 0.45 = 32	$\frac{72}{100} \times 13800 = 9936$
	Methacrylic Acid	4.5	4.5 x 0.50 = 2	$\frac{4.5}{86} \times 15800 = 827$
			663	37547

$$\Delta T = \frac{37547}{663} = 57^\circ\text{C.} \quad \text{Found } 53^\circ\text{C.}$$

b. QUALITY OF WATER

The quality of the water used in emulsion polymerization is important. Polyvalent metal ions present in most natural waters can have a strong inhibitory effect on the polymerization reaction and may lead to flocculation of the polymer emulsion or formulated products manufactured from them. Excessive amounts of univalent ions can also influence formation of micelles and the adsorption of the stabilizing surfactant on the polymer particles. For these reasons, the use of softened or, preferably, deionized water is recommended for the manufacture of emulsion polymers. Deionized water is preferred because the salt content is extremely low, thus permitting the maximum of control on the composition of the emulsion.

3. SURFACTANTS

a. ROLE IN EMULSION POLYMERIZATION

Although the patent literature contains examples of acrylic emulsion polymers prepared without adding emulsifiers, these are customarily employed during the polymerization; further amounts of surfactants are often added to the finished polymer products.

The role of the emulsifier is complex and changes during the various stages of the reaction:

1. Acceleration of Polymerization. Micelles or aggregates formed from the emulsifier solubilize the monomer to provide sites where very rapid polymerization occurs. The surfactant also partially stabilizes the stirred emulsion of monomer droplets. If the unsolubilized monomer formed a separate layer, the rate of reaction would be far less than in an emulsion process because of difficulties in the diffusion of monomer to the reaction sites.

2. Stabilization of Emulsion Product. The surfactant stabilizes the emulsion of monomer-polymer particles and ultimately the final polymer emulsion, preventing the formation of less stable large agglomerates. The rather small quantity of surfactant normally used during the reaction process by no means saturates the surfaces of the

particles. Surfactants are frequently post-added to improve the storage and freeze-thaw stability and to increase the resistance of the emulsion product to the violent mechanical stresses that may occur, for example, in the milling of paints. The post-added surfactant need not be the same as that used during the polymerization.

Despite their obvious importance in the process and final product, surfactants afford a source of weakness in the emulsion product that must be kept in mind. The hydrophilic nature of many emulsifiers used in the polymerization provides a degree of water sensitivity in films of the polymer. The storage stability of many emulsions is also strongly influenced by the type and amount of emulsifier. These contraindicative features must be added to the points considered in deciding on the emulsifier system finally selected for a product.

b. SELECTION OF SURFACTANTS FOR EMULSION POLYMERIZATION

Because of the multiple and contradictory part played by the surfactant, as well as the complexity of the entire system, theoretical considerations offer insufficient guidance in the selection of suitable emulsifiers for emulsion polymerization. For example, those emulsifiers capable of best stabilizing the final emulsion product or even the original monomer droplets are not necessarily the most effective in providing a high reaction rate or low particle size. The most appropriate compounds for the reaction itself seem to be highly hydrophilic materials of the anionic or nonionic classes. Relationships expressing the optimum chemical structure of emulsifiers are difficult to discover. Nonionics having high values of the so-called HLB number (hydrophile-lipophile balance) are usually the best of their class as primary emulsifiers. However, this classification does not apply to anionic materials.

No comprehensive examination of the relationship between the individual chemical structure of emulsifiers and their utility in emulsion polymerization has appeared. Nor should one expect to find such a desirable summary, because it is known that specific interactions may develop between the emulsifier and the other components of the reaction mixture, especially the initiator and the growing particles. While general statements have been made and will be discussed below, these are not necessarily valid for a particular product. This means that selection of a surfactant system usually involves close study in the laboratory (IV-18).

c. IONIC SURFACTANTS

Any of the general classes of surfactants has been used as primary emulsifiers. Cationic surfactants seem to have least interest because they are reported to have adverse effect on the efficiency of the initiators (IV-18,19). Anionics are the most frequently used emulsifiers. Certain alkyl sulfates, arylalkylsulfonates, and phosphates have been recommended as the most effective of their class as primary emulsifiers (IV-19). Many of them have low critical micelle concentrations and are quite active in reducing surface tension and interfacial tension. Relatively small amounts may therefore be used to provide emulsions with very fine particle size (IV-1,20). The viscosity and storage stability of finished emulsions stabilized by anionics may vary with time. This variation is thought to be related to the ionic charge imparted by the emulsion to the surface of the polymer particle; the charge distribution may vary with the structure of the emulsifier (IV-19,21). Because of this charge, anionically stabilized emulsions are inherently sensitive in varying degree to electrolytes, to freeze-thaw cycles, and to the emulsifiers contained in other latexes. This type of latex also tends to form large amounts of stable foam that is troublesome in transfer and formulation. Mixtures of anionic surfactants of different structure have been recommended to overcome some of the shortcomings noted in storage stability (IV-19,21) and foaming (IV-22).

d. NONIONIC SURFACTANTS

The literature reports the usefulness of nonionic surfactants as primary emulsifiers but points to the tendency to the formation of grainy products in their presence (IV-18,19). This has been ascribed to their weaker surface activity and greater difficulty in forming micelles than is observed with anionics (IV-1). Most published studies, however, have dealt with nonionics containing not more than 15-20 polyoxyethylene residues in the hydrophilic segment, hence with HLB values below 16 (IV-23). Recently developed nonionics, including TRITON X-305 and TRITON X-405, intended primarily for emulsion polymerization, contain 30-40 such residues per molecule and their HLB value is between 17 and 18 (IV-23). Although they may not form true micelles easily (IV-24), the large hydrophilic group is associated with a thick atmosphere of water molecules around the aggregates. These aggregates probably resemble micelles in stabilizing and isolating the polymerization sites and subsequent polymer particles, thus providing and maintaining satisfactorily low particle diameters. The hydrated atmosphere around the finished polymer particles also contributes to the stability of the emulsions to electrolytes and freezing.

Mixed anionic-nonionic systems have been recommended frequently for emulsion polymerization. These systems are said to combine the influences of the two classes and perhaps may even exhibit synergistic effects (IV-25). Acrylic copolymer emulsions made with such combinations have been credited with improved freeze-thaw and mechanical stability (IV-26,27,28), stability to electrolytes (IV-28), reduced foaming tendency (IV-29), acceptably low particle size (IV-30), and excellent scrub resistance in paints (IV-30).

e. PROPERTIES OF ROHM AND HAAS SURFACTANTS

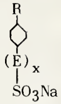
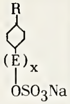
The properties of some Rohm and Haas surfactants suitable as primary emulsifiers are listed in Table IV-4.

f. QUANTITY OF SURFACTANT

In Chapter III, it was shown that the particle size of polymer emulsions is inversely proportional to the concentration of emulsifier. With increasing amounts of surfactant the particle size falls rapidly at first, but soon begins to approach a limit at about 8-10% of emulsifier (based on monomer). Intermediate amounts are therefore used in most cases to give suitably low particle size, rapid rate of reaction, and reasonable stability. The amounts of Rohm and Haas surfactants to be used in acrylic emulsion polymerization have been illustrated in the recipes of Chapter II. About 1-4% of anionics or 2-6% of nonionics (based on monomer) are normally added to provide stable emulsions of fine particle size. When mixtures of these classes are employed, the proportions of each is determined by the effect desired. The salt form of phosphate surfactants also provides some buffering action; polymer emulsions prepared with the sodium salt of Surfactant QS-44, for example, have pH values between 5.0 and 6.5 whereas similar products made with sodium salts of sulfate and sulfonate surfactants may have a final pH of 2.2-2.6. This buffering action may be advantageous during the polymerization of acid-sensitive monomers.

TABLE IV-4

PHYSICAL PROPERTIES OF SELECTED ROHM AND HAAS SURFACTANTS

TRITON	X-305	X-405	CF-32	X-200	X-301	QS-44	QS-10	GR-5
Structure	OPE-30	OPE-40	amine polyglycol condensate			phosphate	phosphate	$COOC_8H_{17}$ $CHSO_3Na$ CH_2 $COOC_8H_{17}$
Solids, %	70	70	95	28	20	80	100	60
Density, lb/gal	9.1	9.2	8.6	8.9	8.8	9.9	9.3	8.4
Viscosity (Brookfield) cps/77°F.[a]	470	490	550	7000		8000	4300	40
Pour Point, °F.	35	25	15	25	30	23	30	-60
Flash Point, °F. (Tag Open Cup)	>300	>212	>300	>300	>300	>175	>175	>130
Acute Oral Toxicity (rats), LD_{50} mg/kg	21000	>28000	9700	17000	27000	4700		
Surface Tension, 0.01%, d/cm	38	48	40	31	31	33^b(0.1%)	27^b(0.1%)	27(1.0%)
Ross-Miles Foam Height at 120°F., mm at 0.1%								
initial	150	126	6	155	150	145^b	70^b	195
5 minutes	113	119	0.2	130	135	125^b	62^b	35
Critical Micelle Concentration, %	ca 0.01	ca 0.1	0.38	0.023	>0.1			0.101
Micelle Surface Area, Å^2		88		45				
HLB Value	17.3	17.9						

a - Varies with rate of rotation and size of spindle   b - At pH = 7.0

As shown in Chapter III, particle size and reaction rate are dependent on the initial concentration of emulsifier. To obtain products of low particle size in a redox process, the entire charge of surfactant is added at the start. If relatively coarse particles are sought, a small portion of the emulsifier is charged at the beginning and the rest is slowly added during the reaction to stabilize the particles (IV-1,18). Extremely fine particles are formed in reflux processes by incremental addition of monomer to the heated emulsifier solution. To avoid the formation of excessive coagulum, it is best to add the monomer as a preformed emulsion using part of the surfactant solution for the purpose (IV-1,18,31). Incremental addition of a preformed emulsion also provides good control of the heat of polymerization.

g. SPECIAL CONSIDERATIONS IN THE SELECTION OF ROHM AND HAAS SURFACTANTS FOR EMULSION POLYMERIZATION

Specialized effects of some Rohm and Haas surfactants may be pointed out. Phosphate types, such as Surfactant QS-44 or QS-10, may require careful attention to the pH and other reaction conditions to avoid highly viscous products (see Chapter II). Phosphate surfactants are very effective primary emulsifiers and the resulting emulsion products are reported to be non-corrosive to metal substrates and give films of high clarity.

Although TRITON X-100 is not usually considered to be a primary emulsifier, it is frequently post-added to stabilize emulsions prepared with anionics (IV-25).

Since one particular advantage of nonionics is their relatively low foam height in comparison to anionics, TRITON CF-32, a surfactant designed specifically for low foam stability, should be evaluated as a secondary emulsifier and stabilizer.

Finally, attention is called to the regulations of the Food and Drug Administration (FDA) that govern the use of surfactants in food packaging applications. Under Food Additive Regulation No. 121 CFR 121.2541 (IV-32), TRITON X-405 has been cleared for use as an emulsifier and/or surface-active agent in the manufacture of articles or components of articles that contact food, including films and coatings for paper. There are many other FDA regulations that pertain to the utilization of Rohm and Haas surfactants in food packaging applications [a].

4. INITIATORS

A very important distinguishing trait of the emulsion process is the use of a water-soluble initiating system. The emulsion system owes its rapid rates and high molecular weight to the separation of the sites where primary radicals form from those where chain growth occurs as well as to the small particle size, both consequences of the use of a water-soluble initiator. Among the water-soluble initiators available at reasonable cost, hydrogen peroxide is not very active in promoting acrylic emulsion polymerization even if an activating substance is present (IV-33,34). Potassium and ammonium persulfates, however, are very efficient catalysts for this purpose and the use of metal ion-activated redox systems increases their versatility. Some preference for the ammonium salt results from its greater solubility and lower formula weight:

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[a] Information on the conformance of Rohm and Haas surfactants with FDA regulations for selected applications is given in Special Products Department Bulletin SP-308.

TABLE IV-5

SOLUBILITY OF PERSULFATE SALTS IN WATER, g/100 g.

	0°C.	20°C.	40°C.	Formula Weight
Potassium Persulfate	1.77	5.3	10.0	270
Ammonium Persulfate	58.2	-	very soluble	228

t-Butyl hydroperoxide is often added as a secondary catalyst to promote complete conversion of the monomer (see Chapter II). The commercial product (IV-a) most frequently used is a mixture of 70% t-butyl hydroperoxide, 20% di-t-butyl peroxide, and small amounts of t-butanol, water, and inert materials. A 90% grade free of di-t-butyl peroxide is also available; it is more stable, hence less easily decomposed than the 70% grade. Although the 70% grade is only sparingly soluble in water (1-5% at 20°C.), this more than suffices for emulsion polymerization; the 90% grade is more soluble (5-15% at room temperature).

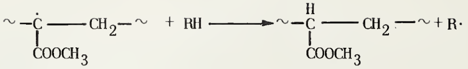
The characteristics of persulfate and redox initiating systems have been discussed in Chapter III, Section C. The usual concentrations are in the neighborhood of 0.01M for persulfate and reducing agent and 0.001M for the ferrous salt. Adequate initiation can be achieved at somewhat lower concentrations of reducing agent. Sometimes complexing agents like the alkali salts of ethylenediaminetetraacetic acid are added to solubilize iron salts above pH 8. Mole ratios of 2/1 for complexing agent/ferrous salt offer sufficient protection against precipitation (IV-35).

Oxygen dissolved in the reaction mixtures inhibits polymerization and must be expelled before the reaction can begin. The presence of oxygen causes wastage of initiator in direct proportion to the amount of oxygen in the system. In reflux processes, oxygen is removed by heating the reaction mixture and the refluxing of monomer vapors provides an inert atmosphere over the reaction mixture. Passage of an inert gas, such as nitrogen or carbon dioxide, displaces the oxygen in a redox process where the temperature is usually too low to cause refluxing of the monomer.

Shipping inhibitors acting together with oxygen effectively stabilize acrylic monomers against unwanted polymerization during storage and transfer. It is reasonable to expect that even small amounts of oxygen can be effective when large concentrations of shipping inhibitor are used and the amount of initiator required to overcome the inhibitor would therefore be relatively large. Low inhibitor grades of monomers should therefore be less subject to interference from oxygen, thus giving short inhibition periods and requiring minimum amounts of initiators.

5. CHAIN TRANSFER AGENTS (MODIFIERS)

Radicals on the growing chains show a far greater tendency to continue reacting with monomer than with other components of a reaction mixture. Nevertheless, reactions of radicals with other ingredients can occur and usually involve attack on a carbon atom bearing a hydrogen or halogen atom. This results in removal (abstraction) of the removable atom which becomes attached to the attacking chain at the site of the former radical and terminates the original growth reaction. At the point where the atom has been abstracted, a new radical site forms, capable of starting a new chain by addition of monomer:



$$\sim\!\dot{C}(COOCH_3)\!-\!CH_2\!-\!\sim \;+\; RH \longrightarrow \sim\!CH(COOCH_3)\!-\!CH_2\!-\!\sim \;+\; R\cdot$$

$$R\cdot + M \longrightarrow RM\cdot \xrightarrow{xM} R(M)_xM\cdot$$

Because of the transfer of the radical from an existing chain to a new one, such reactions are called transfer processes and substances capable of participating in such processes are chain transfer agents. If the chain transfer agent is a foreign substance, that is, not a molecule of monomer or an existing polymer chain, this interruption limits the length to which a chain may grow. The effectiveness of various substances in effecting transfer is expressed as chain transfer rate constants which are very small for most normal ingredients of an acrylic emulsion polymerization.

Certain halogen compounds and especially sulfur-containing compounds are very effective chain transfer agents (Table IV-6). They are therefore capable of modifying the molecular weight of polymer products. The susceptibility of polymers toward transfer increases in the order methyl methacrlyate < methyl acrylate < styrene.

TABLE IV-6

VALUES OF CHAIN TRANSFER CONSTANTS $\tilde{C}_S$ FOR POLYMERS

	Polymer of			
	Methyl Methacrylate		Methyl Acrylate	Styrene
Chain Transfer Agent	60°C.	80°C.	60°C.	60°C.
Carbon tetrabromide(IV-36)	0.27	0.33	0.41	2.2
Ethanethiol			1.57(IV-37)	17.1/50°(IV-38)
Butanethiol	0.66(IV-39)		1.69(IV-38)	22(IV-40)
t-Butyl mercaptan	0.18(IV-39)			3.6(IV-41)
Dodecanethiol				18.7(IV-41)
Thiophenol(IV-39)	2.7			
Ethyl mercaptoacetate	0.63(IV-39)			58(IV-41)

Chain transfer agents do not affect the rate of polymerization of acrylic monomers (IV-41). The values of the chain transfer constants for butyl or amyl mercaptan were the same in bulk and emulsion polymerization of methyl methacrylate as in its copolymerization with styrene. Dodecyl mercaptan was less effective as a modifier in an emulsion process because it diffused with greater difficulty through the aqueous phase into the growing particles.

Because of the special conditions that prevail in the emulsion process, acrylic emulsion polymers normally have molecular weights on the order of 1 million (1×10^6) or more. If a product of lower molecular weight is required, as for example in an application based on ready flow of the polymer, it can be obtained by adding small amounts of efficient chain transfer agents to the reaction mixture. Fryling (IV-43) reported the preparation of soft plastic rubbery polymers from methyl or ethyl acrylate in the presence of 0.3% (based on monomer) of dodecyl mercaptan in an emulsion process. Omission of the mercaptan gave a non-plastic friable poly(methyl acrylate). Butadiene is a monomer that is particularly sensitive to the presence of chain transfer agents, especially mercaptans; they act as polymerization promoters and enhance the rubbery character of butadiene-containing polymers. Copolymers of butadiene with acrylic monomers are often prepared with the aid of mercaptans for the same reasons (IV-28).

A very rough estimate of the molecular weight of a polymer produced in the presence of a chain transfer agent can be made by means of Mayo's equation (IV-44) that assumes a direct proportionality between molecular weight and concentration of the modifier:

$$\frac{1}{P} = \frac{C_S[S]}{[M]} + \frac{1}{P_o}$$

where P and P_o are the respective degrees of polymerization (average number of monomer units per chain) obtained with and without a modifier having a chain transfer constant C_S and [S] and [M] are the molar concentrations of the agent and monomer respectively. Let it be assumed that an acrylic polymer whose normal molecular weight is 1 million (1×10^6) is being prepared in the presence of a modifier having $C_S = 1$. Approximately 0.01, 0.1, and 1 mole per cent (based on monomer) of the modifier are then required to provide molecular weights of 500 thousand, 100 thousand, and 10 thousand, respectively.

A much more rigid treatment from which the effects of chain transfer agents can be deduced is given by Flory (IV-45). If the determination or calculation of molecular weight is inconvenient, an empirical solution for the proper level of modifier can be obtained by testing the product in the desired application. Unfortunately, odor problems may arise when mercaptans or their derivatives are used and halogen-containing compounds may afford polymers that become discolored. The amount of modifier should therefore be held to the necessary minimum.

Transfer processes can also occur with existing "dead" polymer chains. Abstraction of hydrogen from a "dead" chain produces a new site where new growth can occur. If the available monomer is the same as that of the chains, branches are formed. If the monomer is different from the backbone material, the product is a graft copolymer, in which branches of the new polymer are attached to the chains of the old backbone. This is a frequently used and convenient method for the preparation of graft copolymers.

B. REACTION CONDITIONS

1. TEMPERATURE

The general effects of temperature in emulsion processes are similar to those found in homogeneous methods; there are, however, certain aspects unique to the emulsion process. With increased temperature, the overall rate increases and the molecular weight and particle size drop. These results occur as a consequence of several counteracting influences. The overriding factor determining the overall rate is the large increase in the propagation rate constant k_p with increasing temperature (IV-46). Other factors causing a rate increase are the decrease in critical micelle concentration of the emulsifier and the increase in the number of particles. The opposing influence is the small decrease in the monomer-polymer ratio within the particles (IV-47). The decrease in particle size may be as much as 50% for an increase in reaction temperature from 30 to 70°C. (IV-48). The decrease in molecular weight is probably significant, but the molecular weight of emulsion polymers is nevertheless quite high even when made under reflux conditions.

2. EFFECT OF pH

Unlike some other monomers, the pH has little influence in the emulsion polymerization of acrylic monomers. The most important item of concern is in the preparation of copolymers with acrylic or methacrylic acid; the polymerizability of these acids with hydrogen peroxide or persulfate initiators drops sharply above a pH of 5 (IV-49,50). The principal side effect is the possibility of hydrolysis of the ester group of the monomers. At neutral or slightly acid pH, the rate of hydrolysis of methyl or ethyl acrylate, the most easily attacked acrylic monomers, is quite slow even in emulsion systems. The degree of hydrolysis in neutral emulsions of ethyl acrylate at 70°C. is only 0.6% in 6 hours (IV-19). Under alkaline conditions, however, the lower acrylates are saponified very rapidly at room temperature (IV-19). Methacrylates are much more resistant to alkali and the rate of hydrolysis of either acrylates or methacrylates falls off with increasing length of the ester alkyl group.

The saponification of polyacrylates requires far more vigorous conditions and polymethacrylates are attacked only very slowly by moderately strong solutions of acids or bases even at elevated temperatures. Acrylic polymer emulsions can be stored without deterioration over long periods under mildly alkaline pH. When latexes of copolymers containing free carboxyl groups are neutralized, their viscosity increases.

3. AGITATION

Some type of agitation is normally required to break up the monomer into stable droplets, to facilitate diffusion of monomer from the droplets to the growing particles and surfactant from the aqueous phase and micelles to the surface of the particles, and to improve heat transfer throughout the reacting mass. Because relatively little emulsifier is adsorbed on the monomer droplets, they tend to coalesce rather quickly unless adequately strong agitation is provided. Zimmt (IV-51) has found that a separate layer of methyl methacrylate is formed at low stirring rates. The resulting rate of polymerization is then controlled by the rate at which the monomer can diffuse into and through the aqueous phase to the particle sites. Under these conditions the rates were a linear function of time up to conversions above 90% and were considerably below those observed when a stable emulsion of monomer was present. Zimmt also reported that an increase in the stirring rate above a minimum needed to establish the droplets had practically no effect on the rate of polymerization or the particle size.

Stirring is the most commonly used method of agitation for the laboratory preparation of medium to large amounts of polymer emulsions. Small batches of experimental emulsions are made conveniently by shaking or rotating sample bottles. Such a procedure may require less table space per experiment because many samples can be mounted on suitable frames driven by a single motor. Laboratory runs sometimes utilize the stream of inert gas to agitate the reaction mixture. This is helpful in kinetic studies where the data may be vitiated by the entry of even small amounts of air.

Agitation in the plant requires some care to avoid excessive splashing of the reaction charge onto the upper walls of the reactor where gum may form. Care to avoid sucking air into the reactor must be exercised because this can seriously retard the rate of reaction.

In addition, if the peripheral speed of the agitator is great enough, sufficient shearing stress may be applied in the vicinity of the walls to cause the deposition of coagulum by localized breaking of the emulsion. The geometry and placement of agitators and the selection of suitable rotation speeds constitute an empirical art in which adjustments may be necessary to produce high conversion with low formation of gum.

EQUIPMENT SUPPLIER

(IV-a) Supplied by Lucidol Division, Wallace & Tiernan Inc., Buffalo, N.Y. or Shell Chemical Corp., New York, N.Y.

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CHAPTER V

MANUFACTURE OF ACRYLIC EMULSION POLYMERS

A schematic diagram of a plant installation adaptable to redox or reflux processing is given in Figure 5. In the following description of such an installation, specific items of equipment are mentioned because they have given good service in actual use. However, comparable equipment of equivalent quality may be substituted.

A. REACTORS

Industrial acrylic emulsion polymerizations are usually carried out by batch processes in jacketed stainless steel or glass-lined kettles with dished top and bottom heads and designed to withstand an internal pressure of at least 50 psig. Glass-lined equipment is preferred because it is easier to clean. Agitators are constructed from the same materials as the reactor. A suitable agitator is a Pfaudler (V-a) three-pronged curved impeller with a peripheral speed of 150-600 ft./min. Versatility in operating the agitator is achieved by providing a variable speed drive such as a 4:1 Reeves (V-b) Vari-Speed Motodrive. The size of the motor is determined by the capacity of the reactor; the power output may be estimated roughly as 1 hp per 200 gal. of kettle capacity. The temperature of the reactants is controlled by circulating steam and cold water through the jacket, which may be of dimpled construction. Cooling water is best admitted to the jacket through Pfaudler (V-a) agitating nozzles; these produce a turbulent high-velocity stream and are installed easily and inexpensively (V-1). A baffle is sometimes used in the kettle to improve mixing; its width could be about 1/10 of the kettle diameter. The shearing stress produced by the presence of a large number of baffles may be sufficient to flocculate the emulsion product.

A feed line for emulsified monomer is installed to enter through the top. This line should discharge against the wall of the reactor above the liquid level so that the material flows into the reaction mixture as a film rather than as a freely falling stream; this will lessen the tendency to foam or to form coagulum. Nozzles should also be provided in the top of the reactor for adding deionized water, solutions of initiator and activators, and for one-shot additions of various ingredients. Dip pipes should be avoided because gums are easily formed on their inner and outer walls. The accumulated polymer clogs the dip pipe and is hard to remove. Inert gas is best added by bubbling it through a connection on the bottom valve; the use of a sparging pipe is subject to the same objections as a dip pipe.

B. ACCESSORY EQUIPMENT FOR REDOX PROCESSES

1. TEMPERATURE RECORDER

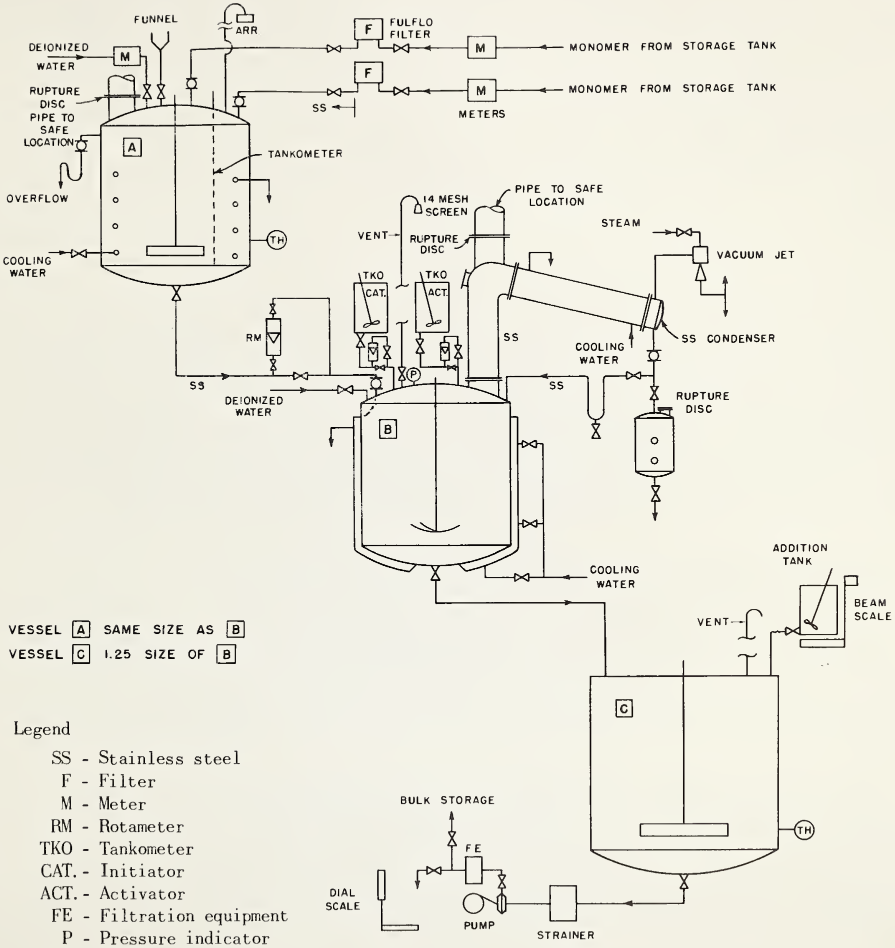
An electronic recorder is preferred for fast response. The temperature probe should extend to near the bottom of the reactor to permit measurement of the temperature at low levels. The probe must be cleansed frequently of polymer deposits to avoid inaccurate readings.

2. MANOMETER or other suitable pressure gauge.

3. MANHOLE AND SIGHTGLASS.

FIGURE 5

PLANT FOR EMULSION POLYMERIZATION



VESSEL A SAME SIZE AS B

VESSEL C 1.25 SIZE OF B

Legend

SS - Stainless steel
F - Filter
M - Meter
RM - Rotameter
TKO - Tankometer
CAT. - Initiator
ACT. - Activator
FE - Filtration equipment
P - Pressure indicator
TH - Thermometer
ARR - Flame arrester

4. EMERGENCY STACK of Spiral-Weld (V-c) pipe or galvanized sheet metal is piped to discharge to a safe location and is fitted at its base with a *rupture disc.* If vacuum is not to be applied, the disc can be cotton impregnated with a phenolic resin such as Synthane Grade L (V-d). When vacuum is required at some stage of the process, as during stripping operations, a disc equipped with a vacuum support must be used. The diameter of the disc is derived approximately from a relationship of the number values of the disc area and kettle capacity. The disc area, expressed as in.^{2}, should be about 1/8 of the kettle capacity expressed in gallons. For example, a 12" disc (area 113 in.^{2}) is used on a 1000 gal. kettle. A *vent pipe* provided with a *flame arrester* is required. Rohm and Haas Co. has obtained satisfactory results by using a simple flame arrester constructed by placing three layers of stainless or aluminum screening over the end of the vent pipe. Such a flame arrester resists plugging by polymer but may not necessarily accord with the regulations of underwriters. Commercially available flame arresters may often be unsuitable because they are easily fouled by vapors of moist monomers and eventually become plugged with polymers. All flame arresters must be inspected at regular intervals for clogging by polymer.

C. ACCESSORY EQUIPMENT FOR REFLUX PROCESSES

The above equipment is used except that a stainless steel stack and a stainless steel *shell* and *tube condenser* are also provided. The stack fitted with a suitable *rupture disc* (see above) is piped to discharge to a safe location; the stack above the rupture disc may be constructed of Spiral-Weld pipe or galvanized sheet metal. The stainless steel shell and tube condenser should have a cooling area in sq.ft. approximately one-fifth of the kettle capacity in gallons. Condensed monomer(s) may be returned to the reactor or discharged to a small *receiver;* if it is returned, the return line should discharge against the wall to form a film rather than a free falling stream. To avoid blockage in the condenser by accumulation of polymer, the vapors should be condensed in horizontal tubes pitched to drain in the desired direction. Refluxing is observed through a *bull's-eye sightglass.*

D. CHARGING EQUIPMENT

Monomer emulsions may be prepared in the kettle or in separate equipment. Although emulsification in the reactor is simpler, pre-emulsification techniques are more efficient and save time when they are used to prepare emulsions for the next batch or for a second stage in a two-stage redox process while the reactants of the first stage are being cooled in the kettle. The pre-emulsification tank is also convenient for continuous charging of monomers in reflux or redox processes.

If the monomer emulsion is to be made in the reactor, the monomer and water are weighed in stainless steel *weigh tanks* fitted with a *dial scale* or other appropriate device for measuring the amount of material. A *measuring tank* with a Tankometer (V-e) is also acceptable. The number and capacity of these vessels is determined by the process requirements. A Rotameter may be used to measure the flow rate of monomer into the kettle or a batching meter can be set to deliver a desired volume of monomer (or monomer emulsion). The quantity of material delivered to the reactor should, however, be checked by the Tankometer or dial scale on the tank.

Stainless steel pre-emulsification tanks should have adequate capacity to permit the preparation of the monomer emulsion. For a single-stage process, for example, the capacity would be comparable to that of the kettle. In multi-stage processes, the capacity could be correspondingly reduced, but a large tank capable of holding the entire batch would, of course, allow the maximum flexibility in operation. The pre-emulsification tank is usually equipped with a *turbine agitator, manometer level gauge, cooling coils,* a *sparger* for inert gas, *thermometer* or *temperature recorder,* Synthane Grade L (V-d) *rupture disc, flame arrester,* and various nozzles for charging the ingredients. Deionized water and monomers are charged by gravity or pumped into the pre-emulsification tank through a stainless steel *cartridge filter* and stainless steel lines. Upstream of the filter, acrylates and methacrylates may be transferred through mild steel lines, but stainless steel lines are used between the filter and the kettle. Glacial acrylic or methacrylic acids must be moved through stainless steel lines. Suitable filter units are the Fulflo (V-f) stainless steel type (typical model numbers are indicated below) fitted with cartridges of cotton wound on a stainless steel case (Commercial Filters Corp. code 19X10-2SV) capable of removing particles having diameters as small as 7 microns. The pressure drops of filter units, which depend on the number of cartridges, are:

Fulflo Model No.	Number of Cartridges	Pressure Drop, psi at 50 gal/min
WYFSS-10-1-1/2	6	4
WYFDSS-10-1-1/2	12	0.7

The monomer emulsion may be charged in one shot to the reactor or transferred continuously through a meter as described above.

Aqueous solutions of initiators and activators are mixed separately in buckets or bottles and added directly to the kettle or through stainless steel lines. In more elaborate installations, as illustrated in Figure 5, these solutions are made up in stainless steel *tanks* mounted on a weighing scale and fitted with a level gauge, Rotameter, and stainless steel needle valves. Surfactants are weighed and charged directly to the kettle or to the pre-emulsification tank.

Although gravity feeding is often used to transfer ingredients or pre-emulsions, stainless steel centrifugal pumps are also utilized for this purpose. The pump capacity is determined by the type of process; in redox processes, materials are added rapidly because the reaction cannot proceed until the initiating materials have been added and the heat of polymerization is absorbed by the aqueous phase. Since heat removal is the limiting factor in reflux processes, a pump providing a low feed rate may be adequate.

E. DRUMMING EQUIPMENT

A simple stainless steel *drumming tank* is used to receive the polymerized emulsion and to hold it until it is loaded into drums. This tank is also employed to adjust the solids content and pH, for the addition of preservatives, stabilizers, and thickeners, and for blending batches. A paddle type low speed (about 20 rpm) agitator is used for mixing and cooling; adjustable baffles are sometimes installed for more efficient mixing. A small mixing tank may be provided to allow addition of small quantities of additives. A cooling jacket on the drumming tank permits the finished emulsion to be discharged hot from the reactor, thus increasing the production capacity of the kettle. To minimize the formation of foam during the discharging of the batch, a long polyethylene "sleeve" made from film supplied in long rolls is attached to the discharge line and the material falls into the drumming tank below the surface; the sleeve is discarded after the kettle is emptied. A burlap bag or piece of cheesecloth may be placed over the end of the discharge line to remove coagulum. The cooled finished polymer emulsion is strained again through a cheesecloth filter bag or a coarse Fulflo filter while loading drums by gravity or through a basket screen on the suction side of pumps when they are used (see Chapter VI, Page 55). Clogged filter bags or filter cartridges are discarded and replaced. Skin may be burned off metal screens or removed from metal or plastic screens by backwashing.

F. WATER SUPPLY

An adequate supply of deionized water[a] for the reaction mixtures and of cooling water for the jacket, cooling coils, and condenser must be provided.

Refrigeration equipment (V-g) may be required during warm weather to supplement the cooling water. Although no reliance may be placed on the cooling water to control the reaction temperature of redox processes, it can reduce the temperature before adding the initiator or after the reaction is completed. Refrigeration capacity depends on local conditions and on the speed with which it is desired to bring about the necessary cooling. The size of a refrigeration plant is therefore governed by economic as well as technological conditions.

G. PLANT SCALE OPERATION

The processing conditions of bench-scale operations are in general adaptable to large-scale production and laboratory methods similar to those described in Chapter II are readily scaled up to plant-size batches. Many adjustments in charging and heating schedules and in methods of feeding reactants and of agitation may be required to establish efficient processes and to provide good yields of products possessing satisfactory reproducibility, stability, and performance. Changes in the recipe may require confirmation of adequate performance in applications and should be backed up by preliminary study in the laboratory. Safe operating procedures cannot be overemphasized and process conditions must permit control of the highly exothermic polymerization reactions at all times. It should be kept in mind that the liberated heat is disposed of by absorption in the aqueous phase in a redox process and by condensation of vapor and circulation of cooling water in a reflux process. The correct ratio of monomer to water must not therefore be exceeded; when monomers are added during the period of active polymerization, the feed rate must be maintained below the capacity of the heat-absorbing mechanisms. Reasonable cleanliness in the equipment is also necessary; it is particularly important to keep temperature probes, cooling and heating coils, and condenser tubes as free as possible of deposited polymer. Personnel responsible for the supervision and operation of acrylic polymer emulsion plants should be thoroughly familiar with the preferred methods for safe storage, handling, and transfer of acrylic monomers and other ingredients[b].

H. REMOVAL OF RESIDUAL MONOMER

Although the polymerization of acrylic monomers is essentially quantitative under normal circumstances, the removal of small amounts of residual monomers may sometimes be required.

[a] Information on the deionization of water is available from qualified suppliers of water-conditioning equipment or the Ion Exchange Department, Rohm and Haas Co.

[b] An excellent discussion of the procedures and equipment for storage and handling of acrylic monomers is given in the Special Products Department Bulletin SP-130. Similar information on Rohm and Haas surfactants is available in various product bulletins of the Special Products Department, especially Bulletin SP-323. Information on LYKOPON and FORMOPON is given in Bulletin SP-21. Suppliers of persulfate and peroxides should be consulted for their recommendations on handling their products; brief helpful comments are found in Bulletin SP-159.

In addition, partial evaporation of the water phase may be desired to increase solids content and to destroy vestiges of the initiators.

Stripping and evaporation are carried out by post-heating the batch at temperatures and pressures consistent with the foaming tendency and stability of the emulsion. Many acrylic polymer emulsions can withstand heating at 95-97°C. without being flocculated. The emulsion is heated by circulating low pressure steam in the jacket. The degree of foaming is observed through a sightglass on the reactor manhole or by a glass-coated or Teflon-coated probe (V-h) (V-2). Excessive foaming is controlled by the degree of vacuum or, in an emergency, by quenching with cold water from a line feeding directly into the reactor. Vacuum should be withheld until the kettle contents have been heated to the desired temperature and is then applied gradually. Foam knockout vessels have also been recommended (V-3) for the control of foaming in emulsions. Antifoam agents may be helpful in some instances but their effect on the properties of the emulsion should be checked. The final removal of monomer is indicated when separation of the strippings into oil and aqueous phases no longer occurs upon observation through a sightglass on the receiver. An inhibitor should be added to the receiver before beginning the stripping operation. Even though it contains inhibitor, recovered monomer is unstable and should be destroyed promptly by burning, by cautious addition to dilute alkali solutions, or by disposal in a trickle filter[a].

Commercial equipment is available for the continuous stripping of residual monomers from acrylic polymer emulsions. The units may also be used to concentrate latexes to higher solids content. Information on this system can be obtained from the manufacturer (V-i).

I. CLEANING EQUIPMENT

The reactor, mixing tanks, and drumming tanks should be rinsed with water after each use to remove polymer before it has a chance to dry. Despite all efforts, deposits of polymer will gradually build up and will eventually require removal. They can be loosened and partially removed from the reactor by several hours of vigorous boiling with water. More adherent films may necessitate boiling with 1-3% aqueous ammonia or, in stainless steel vessels only, with dilute caustic solutions. Any remaining solid must then be lifted manually with any type of scraper that will not damage the surface of the reactor. After cleaning, the reactor is flushed with clean water. Deposits form gradually in the drumming tanks and are removed manually. Pumps and lines should not require cleaning if they are properly drained and flushed.

EQUIPMENT SUPPLIERS

(V-a) Pfaudler Co., Division of Pfaudler Permutit Inc., Rochester 3, N.Y.

(V-b) Reeves Pulley Co., Division of Reliance Electric & Engineering Co., Columbus, Ind.

(V-c) Taylor Forge and Pipe Works, Chicago, Ill.

(V-d) Black, Sivalls, and Bryson Inc., Kansas City, Mo.

(V-e) Uehling Instrument Company, Patterson, N.J.

(V-f) Commercial Filters Company, Melrose 76, Mass.

(V-g) Worthington Corp., Harrison, N.J., or Ingersoll-Rand Company, New York 4, N.Y.

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[a] Information on the construction and performance of trickle filters for waste disposal is available on request to Special Products Department.

(V-h) Robertshaw-Fulton Controls Company, Aeronautical & Instrument Division, Anaheim, Calif., or Compudyne Corp., King of Prussia, Pa.

(V-i) Parkson Industrial Equipment Co., Fort Lauderdale, Fla.

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CHAPTER VI

STORAGE AND TRANSFER OF ACRYLIC EMULSION POLYMERS

Emulsions are inherently subject to various manifestations of instability common to all colloidal systems. This characteristic is necessary in using them, but must be controlled during storage, since they may become unsuitable for the application. Undesirable changes may be incited by time, by drift in pH, evaporation, high temperature or freezing, shear and turbulence, movement of air bubbles, and foaming. The common designations for these changes are layering, skinning (surface film), gritting (solid within the emulsion), gumming (deposits on walls), and sponging (formation of an aerogel during foaming). Oxidative degradation is not usually encountered with acrylic polymer emulsions, but bacterial attack is common and is avoided by adjustment of pH, addition of bactericidal agents, and careful housekeeping.

In general, emulsion polymers should be handled gently, used in a relatively short time, and protected from changes in composition and from harmful external conditions and materials. The cleanliness of process and storage equipment should be maintained by regularly established routines.

Emulsions are shipped in bulk or in drums. *Tank trucks* and *tank cars* used for bulk shipment are constructed of stainless or resin-coated steel and are insulated to prevent freezing of the contents during long trips in cold weather. *Drums* are 50-55 gallon capacity fiber containing a liquid-tight duplex polyethylene barrier or semi-rigid polyethylene liner (VI-1); open- or closed-head coated steel containers may also be used.

Tank cars can usually withstand 10-15 lbs. of pressure, and compressed air may be used to empty them. Tank trucks are ordinarily not designed to withstand more than 1 or 2 lbs. pressure although some capable of withstanding 25 lbs. are available. They are usually emptied by gravity or pumping, methods also preferred for discharging cars. Frozen emulsions in cars may be thawed by circulation of hot water, *but not steam,* through the coils. However, many emulsions are destroyed by freezing, and freezing of acrylic emulsion polymers capable of surviving several freeze-thaw cycles should nevertheless be avoided. Drained trucks and cars should be rinsed promptly and a shallow pool of clean water left within them for the return trip.

The essential equipment for a suitable indoor storage installation is shown in Figure 6. Storage tanks may have dished top and bottom heads or flat sloped bottoms to permit complete drainage and are preferably made of stainless steel (304 or 316). Stainless tanks are very durable, easily cleaned, and harmless to emulsions. Aluminum, glass-lined steel, glass-reinforced polyester, and phenolic-coated steel tanks are also satisfactory in many cases. Aluminum can be pitted by some emulsions and darkened by others. Glass reinforced polyester tanks formulated by reputable fabricators from Atlac 382 polyester resin (VI-a) are suitable for the majority of acrylic emulsions. Phenolic coatings like Heresite (VI-b) have given good service although periodic renewal is usually required (VI-2). Resin coating should be applied by experienced approved applicators. Freezing in *outdoor* tanks may be prevented by installation of a *heating coil* in the tank pad for circulation of hot water. A *jacket* is preferred but is, perhaps, more costly. *Outdoor* tanks should be fully insulated.

The various accessories required for storage tanks include the following:

1. AGITATION. Although many acrylic emulsions require no agitation under normal conditions of storage, some must be agitated rather frequently to ensure homogeneity. In these cases, a *vertical overhung-shaft agitator* of about 8 rpm with large paddles driven

FIGURE 6

TYPICAL BULK STORAGE FOR ACRYLIC POLYMER EMULSIONS (INDOORS)

NOTE

1. Pitch all emulsion lines for ease in draining.
2. Outdoor tanks require insulation, coils or jackets for heating, and a temperature controller.

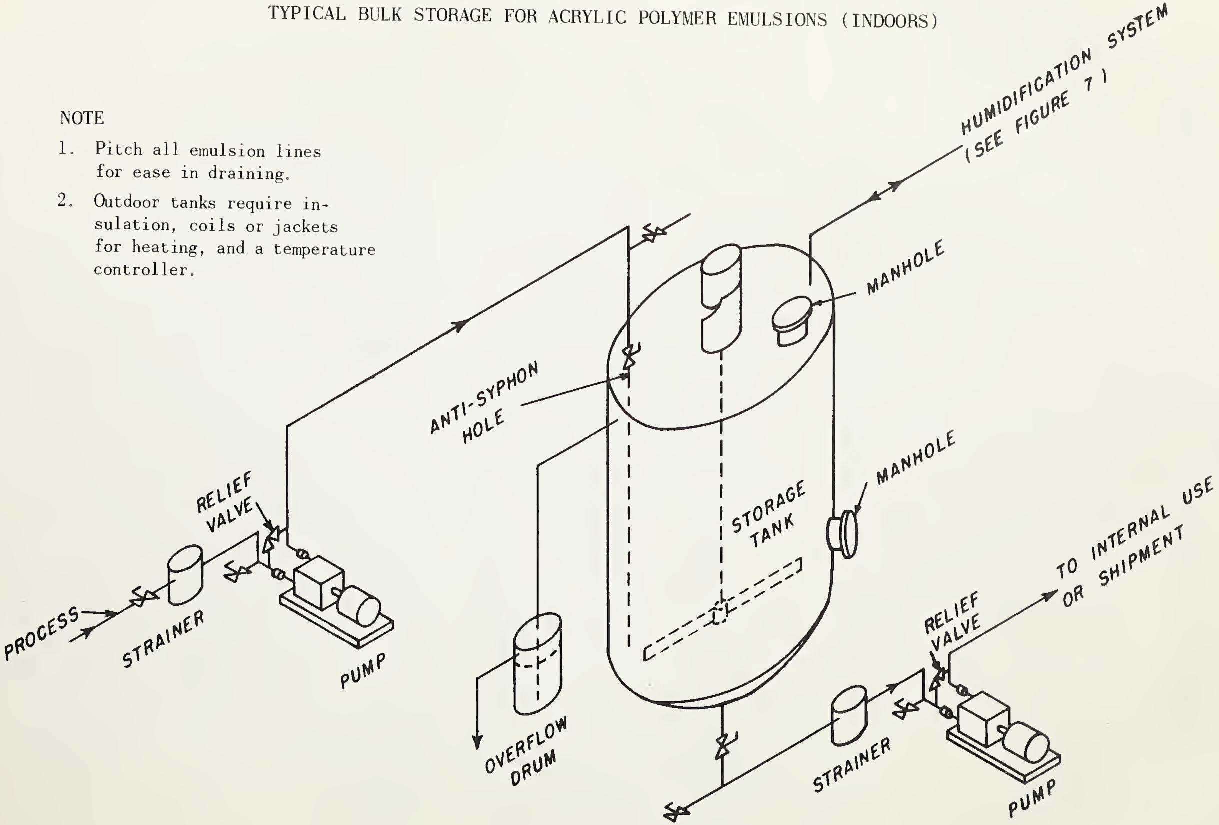


FIGURE 7

Wet Breather Systems for Acrylic Polymer Emulsion Storage Tank (Indoors)

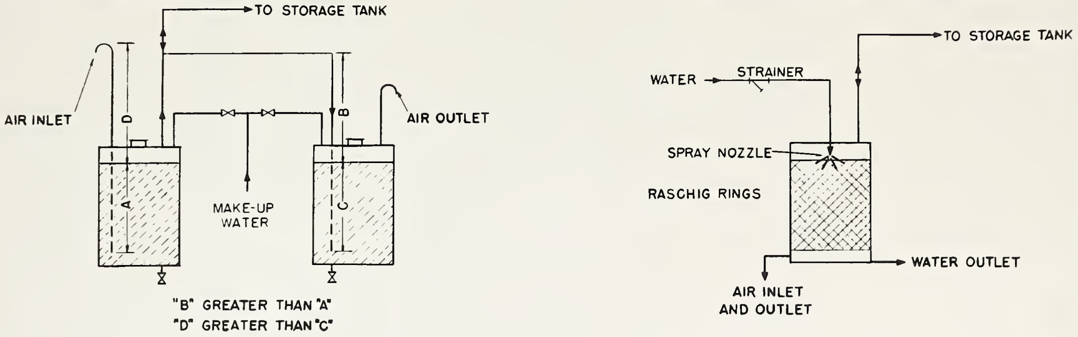


DIAGRAM A

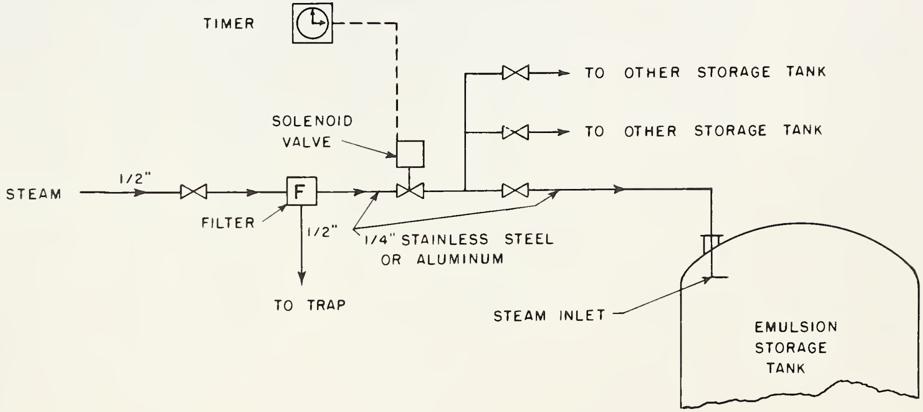
USING TWO WATER FILLED DRUMS

DIAGRAM B

USING WATER SPRAY IN PACKED COLUMN

DIAGRAM C

Using Steam Humidification System



at a peripheral speed of not more than 200 ft/min. is best. Side-entering mixers of 300-500 rpm are suitable for brief intermittent mixing. Recirculation with a low-speed centrifugal pump is less desirable but may be used with several inlets at various levels to insure proper mixing. Intake of air should be avoided with all devices.

2. MANHOLE WITH REMOVABLE COVER facilitates cleaning. Tanks should be cleaned periodically with water and low-pressure steam. Steam nozzles should be used carefully to avoid damage to coatings in resin-coated tanks. The flushed tanks may then be entered and deposits of film removed by hand or by scraping with a rubber or plastic tool. To avoid growth of microorganisms, tanks and lines should be drained and steamed periodically for at least one hour.

3. DOWNPIPE of stainless steel extending to within six inches of the tank bottom, with a hole near the top to prevent siphoning, is required. These holes may become inoperative if they become plugged; care should therefore be taken to avoid a condition that could cause siphoning. Filling below the surface is necessary to avoid the formation of air bubbles and foaming. Storage tanks may also be loaded from the bottom if provisions are made to prevent accidental loss of the tank contents.

4. PIPELINES are preferably stainless steel and of adequate size. Steel pipe lined with polypropylene (VI-c) or high density polyethylene, aluminum, and reinforced plastic pipe, such as Fibercast pipe (VI-d), may also be used. Aluminum or Fibercast pipe may not be acceptable for specific emulsions and should be checked before use. If rusting and a considerable amount of building on the walls can be tolerated, steel pipe may be utilized. Plastic pipe should be capable of withstanding steaming unless some other means of combatting bacterial growth is applied. Galvanized steel or poly(vinyl chloride) (PVC) piping are not recommended. Outside lines should be insulated and may be traced with electrical heating cables when permitted by local Electrical Codes. All pipes should be pitched for good drainage and be easily accessible and flanged for cleaning. They should be provided with valves to admit water for flushing immediately after use.

5. PLUGCOCKS should be Teflon-lined non-lubricated stainless steel, poly-propylene-coated steel, or Saran-coated steel. Teflon-lined *ball valves* of acceptable design are also useful. *Diaphragm valves* of similar materials, in which the diaphragms are of neoprene, Buna N, or other similar synthetic elastomers, are satisfactory.

6. BASKET STRAINERS of adequate capacity fitted with 14-mesh screening are placed at appropriate spots in the system to remove large gum and other solid particles.

7. A WET-BREATHER system is used to saturate the air entering the tank during transfers. Any of the three systems shown in Figure 7 is satisfactory and can be operated manually or automatically; several tanks in parallel can be serviced by a single wet-breather system.

Diagrams A and B illustrate methods of saturation with liquid water. In Diagram A, the air is bubbled through water-filled drums, and in Diagram B the air is saturated with a water spray in a column packed with Raschig rings.

Diagram C is a sketch of the preferred system in which steam is injected directly into the storage tank. Although the best procedure would be to add steam for about 10 seconds after each withdrawal from the tank, it is simpler to humidify automatically for about 20 seconds every 8 hours. The steam flow may be controlled by a solenoid valve actuated by a timer. Steam is projected horizontally across the vapor space from one side of the tank and should flow until it can be seen to emerge from the tank vent. Although condensation undoubtedly occurs within the tank, dilution of the emulsion has not been observed. A filter and trap assembly is used in the steam feed line to prevent entry of dirt, scale, and condensate into the tank. A satisfactory filter unit is the Fulflo (VI-c) Model SS 4.5C10-3/4 containing a reusable sintered stainless steel cartridge Model 5PM10. The bottom of the casing of the filter unit is fitted with a steam trap to remove condensate. Piping from the filter to each tank should be 1/4 inch stainless steel or aluminum, insulated, and as short as practicable. The 15 psig or higher steam supply flows through a 1/2 inch mild steel line to the filter and steam trap.

8. HERESITE-COATED DIAPHRAGM PUMPS (VI-f) provide gentle pumping action and delivery pressures up to 100 psi but are rather bulky and expensive and deliver a pulsating flow. Moyno progressive cavity pumps (VI-g) with water seals are equally effective for handling shear-sensitive emulsions and are usually less expensive. Construction should be of stainless steel with Buna N or butyl rubber liners. Stainless steel *centrifugal pumps* or *gear pumps* may be used for emulsions with sufficient resistance to shear. Centrifugal pumps should be open-type with large clearances, relatively slow-speed (1750 rpm preferred), water-sealed to exclude coagulum from the packing, and easily disassembled for cleaning.

Pumps should always be operated under conditions of flooded suction rather than suction lift. Working under vacuum must be avoided to prevent sucking in of air bubbles. The line on the suction side should be of ample size, short, and as free of bends as possible, fed by a sufficient head of gravity and protected by an adequate strainer.

9. WEIGH SCALES are suitable for process feeding. A *disc meter* (VI-h) or an oscillating piston meter (VI-i) are also satisfactory if deposits of gum can be avoided. Flow meters such as Rotameters should be avoided.

10. VAPOR-TIGHT FLOAT LEVEL INDICATORS (VI-j) are automatic devices for indicating the level of tank contents. However, *stick* measurements are usually used. Manometer-type gauges and similar instruments are usually unsatisfactory because of excessive gumming.

Loading of shipping containers from reactors or tanks requires similar equipment for transfer operations. Containers should be filled as completely as possible to avoid sloshing in transit (VI-3).

EQUIPMENT SUPPLIERS

(VI-a) Atlas Chemical Co., Wilmington 99, Del.

(VI-b) Heresite and Chemical Co., Manitowoc, Wisc.

(VI-c) Saran Lined Pipe Co., Ferndale 20, Mich.

(VI-d) Youngstown Sheet and Tube Co., Youngstown, Ohio.

(VI-e) Commercial Filters Co., Melrose 76, Mass.

(VI-f) T. Shriver and Co., Harrison, N. J.

(VI-g) Robbins & Myers, Inc., Moyno Pump Division, Springfield, Ohio.

(VI-h) Neptune Meter Co., Long Island City 1, N. Y.

(VI-i) Badger Meter Manufacturing Co., Milwaukee 23, Wisc.

(VI-j) Vapor Recovery Systems Co., Compton, Calif.

REFERENCES

(VI-1) T. E. Dowling, Containers for Chemicals, Chem. Eng. **67** (19), 85 (1960).

(VI-2) Rohm and Haas Co., Resins Department Bulletin AP-25-57 gives details of a method for recoating tanks.

(VI-3) S. J. Baum, Ind. Eng. Chem. **49**, 1797 (1957).

CHAPTER VII

TEST METHODS FOR THE EVALUATION OF ACRYLIC POLYMER EMULSIONS

Methods for the evaluation of acrylic emulsion polymers are used to study the efficiency and reproducibility of laboratory and plant preparative processes, to indicate the effects of added chemicals and of storage and handling, and to determine their suitability in applications. Among the tests applied routinely to monitor laboratory studies or plant production, the measurement of solids content, pH, viscosity, shelf stability, and residual monomer are perhaps the most important. Other methods are more often employed during the development stages for new or improved products. These more specialized studies may demonstrate advantages or difficulties in formulation and point out relationships between the composition and properties of emulsion polymers and the requirements of applications. Since the details of the various procedures may differ for specific products, the present discussion is largely confined to a description of their essential features and usefulness. Additional information is available in the reference publications cited below.

A. EVALUATION OF LATEXES

1. SOLIDS CONTENT

This method is used to determine the conversion of monomer and the yield of polymer and also provides a basis for formulation work. A small tin dish (VII-a) held within a tin box covered by a tight lid (VII-b) is dried to constant weight in a forced draft oven at 150°C., cooled in a dessicator, and tared. A sample of appropriate size is then weighed into the dish and the assembly is heated as before for 20 minutes; the lid is held ajar to permit escape of volatile materials. An infrared lamp may be used to dry the sample. After cooling for 30 minutes in an empty dessicator, the tin dish is reweighed; the ratio of residual solid to the original weight gives the solids content. The time and temperature of heating may be modified to accommodate various polymers. When the determination is used to follow the course of polymerization, a shortstopping agent like sodium dimethyldithiocarbamate may be added to a sample to prevent further reaction.

2. pH

An order-of-magnitude measurement can be made with test papers. For precise work, a conventional pH meter with glass and calomel electrodes standardized against a buffer solution is employed. The surfactants in the emulsion may cause some needle drift.

3. VISCOSITY

For most acrylic emulsion polymers, the Brookfield viscosimeter is satisfactory and can measure viscosities up to 100,000 centipoises. This device has interchangeable spindles which are rotated at given rates within the emulsion. The viscosity is then obtained by comparing the dial reading to a calibration curve furnished by the instrument manufacturer. For significant comparisons between various products, the same spindle and rate of rotation should be used.

4. RESIDUAL MONOMER

Under normal conditions of production, the conversion of acrylic monomers to polymers in an emulsion process is practically quantitative. If the usually low concentration (below 1%) of unconverted monomer is exceeded, difficulties with emulsion stability and odor may occur. The lower-boiling acrylic and non-acrylic monomers can be steam distilled by evaporation of the diluted emulsion and collection of a standard amount of distillate. Monomeric acrylic esters in the distillate are then saponified with alcoholic potassium hydroxide at room temperature or under reflux for the more resistant esters. The consumption of alkali is finally determined by titration of the excess. The method is not specific since it does not distinguish between the various acrylic esters or vinyl esters which may be present. The diluted emulsion must be neutralized carefully to prevent volatilization of acidic or basic substances which may interfere with the subsequent titration.

Instrumental methods can be applied to the determination of residual monomers in emulsion polymers. The fastest procedure utilizes gas-liquid chromatography; a sample of emulsion is injected into the entry port of a chromatographic column. The chromatogram may be developed by a thermal conductivity detector, or, more sensitively, with a flame ionization detector (VII-1). This method is specific and quantitative for individual monomers alone or in mixtures. Standard monomer emulsions are used to calibrate the specific retention times and peak areas or peak heights for the component. With a flame ionization detector, the interference of water, the principal volatile component of all emulsion polymers, is overcome by using methyl ethyl ketone or benzene (VII-2) or isobutyl acetate[a] as an internal standard. In another method, the interference caused by water is eliminated by reacting the latex with acetic anhydride or 2,2-dimethoxyethane (VII-3).

5. MECHANICAL STABILITY

Emulsions are often sensitive to the shearing stresses encountered during motion as in agitation, pumping, milling, spraying, and shipping. A rapid measure of mechanical stability is obtained by screening a sample through a 100-mesh screen, then stirring it at high speed in a Waring Blendor for 5 to 10 minutes. The emulsion is again passed through the screen and washed through with water until only solid, if any, remains on the wire. If there is no solid residue, the emulsion is considered to possess very satisfactory mechanical stability. If desired, the amount of solid can be weighed after drying the screen in a circulating draft or vacuum oven at 80-100°C.

6. SHELF AND THERMAL STABILITY

The normal appearance of polymer emulsions may vary from very thin opalescent milks to thick smooth creams depending on the particle size and solids content. On standing, separation into phases, deposition of solids, or darkening in color may occur; foaming may be observed during transfer. The shelf life during prolonged storage or at elevated temperature can be observed by visual inspection or by measuring changes in viscosity. ASTM D1849 describes investigations of shelf stability of latex paints based on changes of Stormer viscosity.

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[a] Information on isobutyl acetate as internal standard in the GLC determination of residual monomers in acrylic emulsion polymers is available on request from the Special Products Department.

7. FREEZE-THAW STABILITY

Although many commercial emulsions are coagulated by freezing, freeze-thaw stability is nevertheless a desirable property which is easily measured. The exact test conditions may be varied to suit the conditions expected to be encountered in actual use. A typical cycle involves freezing at 5°F. (-15°C.) for 16 hours, followed by thawing at ambient temperature (70-80°F.). The cycle may be repeated as often as required; stability after 5 such cycles is normally considered satisfactory.

8. COMPATIBILITY

In compounding various products, acrylic polymer emulsions may be mixed with other emulsion polymers as well as with salts, surfactants, pigments, and other substances. Emulsion polymers may come into contact with various substances contained in the materials to which they are applied. The latexes may be coagulated wholly or partially or be incompatible with some of these substances.

To determine their effect on stability, solvents, solutions, or dispersions are added dropwise to the gently stirred emulsion and any changes in appearance and consistency are noted. Compatibility ratings for mixtures of emulsions are obtained by coating and drying a thin film of the mixture, as well as the original emulsion for comparison, on glass. The dried film may be removed from the glass for examination. If the film is entirely clear and remains so after stretching, bending, or folding, the substances are considered to be entirely compatible. If opacity is developed by working the film, the materials are rated marginally compatible. Varying degrees of incompatibility are indicated from the appearance of the unworked film which may range through degrees of cloudiness or haziness to a completely opaque or even cheesy structure. In many applications, marginal compatibility is acceptable; for example, complete film clarity may not be required in a paint or other pigmented formulation.

9. PARTICLE SIZE AND PARTICLE SIZE DISTRIBUTION

In the laboratory it is possible to obtain polymer emulsions having very narrow ranges of particle sizes by careful control of conditions. In practice, however, polymer emulsions are polydisperse, that is, they contain a more or less broad range of particle sizes. The most important effect of particle size is on the viscosity of the emulsion. Large particles are, in general, associated with low viscosities. Furthermore, a large difference between the diameters of the large and small particles is reported to be required for low viscosity (VII-4). Particle size distributions are also important in the study of the mechanism of emulsion polymerizations (VII-5,6).

Because of the existence of polydispersity, several methods for measuring particle sizes may be required to give complete information. For purposes of comparison, however, the application of a single procedure may often be adequate. Another complicating factor is the frequent formation of agglomerates which may behave like large particles under use conditions. Not all methods can account for the effect of agglomeration on particle size (VII-7). The following sections present brief descriptions of the most important procedures.

a. ELECTRON MICROSCOPY (VII-7,8)

Particle size is often obtained from electron microscope measurements. The method is accurate, gives a visual picture of the particles, and permits measurements on individual particles. The method is most effective with properly prepared specimens of polymers which are not deformed by the heat of electron beams. Diffuse images are frequently obtained from film-forming polymers because of deformation during the drying processes required in the preparation of the material for microscopic examination. Special techniques are then required to prevent the distortion of the particles. Other drawbacks of electron microscopy are the relative expense of the instrumentation, the skill required in the preparation of specimens, and the failure to account for agglomeration. Counting of the particle size is tedious and time-consuming, but instruments such as the Carl Zeiss Model TGZ-3 Particle Size Analyzer (VII-c) are available to improve the precision and decrease the time required for the count. A description of a similar analyzer and its operation has been published (VII-9).

The diluted latex is dried down on a suitable substrate and a protective, heat-conducting coating of carbon or metal is applied in a vacuum deposition apparatus. Electron microphotographs are then obtained at very high magnification and a count of particle size is made. A bar plot (histogram) of the number fraction of particles between two radii is a convenient representation of the data. By applying conventional equations of statistics, various average radii, such as the arithmetic mean or number average, surface average, and weight average can be calculated.

Exposure of a poly(ethyl acrylate) latex to radiation from a van de Graaff accelerator has been utilized to harden the particles before preparing the specimen (VII-10). A variation of this procedure involves the irradiation with X-rays of monomeric styrene sorbed on the particles; a much smaller radiation dose can be used to set the film than would be required for crosslinking (VII-11). Filmforming polymers can also be handled by applying the latex to a substrate carrying monodisperse spheres of polystyrene and shadowing the resulting film. From measurements of the apparent particle diameter and the length and angle of the shadows, the original diameter of the soft particles can be calculated with reasonable accuracy. This technique has been applied to a 2:1 copolymer of ethyl acrylate and methyl methacrylate (VII-12).

b. ULTRACENTRIFUGATION (VII-13)

Measurements of particle size distribution by sedimentation procedures are based on the principle that the larger particles settle out faster than smaller ones when a gravitational force is applied to an emulsion. To accelerate the settling process, the force is applied by an ultracentrifuge; a suitable instrument is the Spinco Model L Ultracentrifuge (VII-d). The fractional loss in solids content at a given location in the centrifuge tube is determined at intervals. The weight fraction of particles larger than a given radius r_c is calculated from Stokes' law:

$$r_c^2 = \frac{9\mu \ln(S+X)/S}{2\omega^2 t(\rho-\rho_o)}$$

where η = viscosity of water
ρ, ρ_o = density of polymer and water
ω = angular velocity
t = time of centrifugation
S = distance from top of the cell to the axis of rotation
S+X = distance from sampling point to the axis of rotation

The density ρ must be different from the density of water and should be measured accurately. It can be estimated from the density and solids content of the latex and the density of water, assuming additivity of the volumes.

A latex is diluted to about 3% solids and the exact solids content c_o is determined gravimetrically. After centrifugation at constant rate for a given time, a small sample is removed from a specified location in the tube for redetermination of solids content c_ω. The measurements are repeated at several time intervals and speeds of rotation. The ratio c_ω/c_o gives the weight fraction of particles of r_c or less. From a cumulative plot of C_ω/C_o and r_c, the weight fractions of particles between given limits of radii and the weight average radius can be calculated.

The method is simple in operation and can be applied equally well to hard and film-forming polymers and to agglomerating polymers for the determination of weight average radii. Accurate values of number average radii, however, are not obtained.

c. SOAP TITRATION (VII-14)

A diluted latex is titrated with a soap solution of known concentration and the surface tension is measured after each addition. With increasing concentration of surfactant, the surface tension drops until a constant value is attained at the critical micelle concentration. The slope of the surface tension vs. surfactant concentration plot is equal to the moles of soap adsorbed per gram of polymer. It is convenient, though not necessary, to use the same surfactant in the titration as in the preparation of the emulsion to simplify the calculations. If this is done and the original amount of soap per gram of polymer solids is known, the surface area per gram of polymer can be calculated and hence the surface average radius of the polymer particles.

Soap titrations are rapid and reasonably accurate and utilize inexpensive equipment. The effective surface area of the soap titrant must be measured. This can be calculated from the Gibbs adsorption isotherm obtained from measurements of the interfacial tension of water-hexane mixtures at various concentrations of soap. The following values of effective surface areas for some common surfactants have been determined in this way:

Sodium lauryl sulfate	61 sq. Angstroms
TRITON X-202	62 sq. Angstroms
TRITON X-405	88.5 sq. Angstroms

d. LIGHT SCATTERING MEASUREMENTS (VII-7,15)

A beam of light is passed into a sample of diluted latex in a photometer cell. The intensity of light scattered by the polymer particles at various angles from the incident beam and at various solids contents is determined. The angular dependence of the intensity is a function of the particle size, the wavelength of light, and the relative refractive indices of the liquid and polymer. Although the method is rapid and simple, it is subject to serious errors when applied to polydisperse systems because of heavy weighting of the larger particles. There are many variations of this procedure and a simplified approach can be used for the qualitative comparison of polymer emulsions having closely similar composition.

e. FRACTIONAL CREAMING (VII-16)

In the presence of a given concentration of sodium alginate, only particles above a certain critical size are creamed. A latex is diluted to 2.5% solids content in the presence of 4% soap and various concentrations of sodium alginate. Samples of the creams are skimmed and their solids contents are determined. The weight fraction, M_α, of particles below a given size corresponding to the concentration of alginate is calculated from the following equation:

$$M_\alpha = \frac{c(1-C_o)}{c_o(1-C)}$$

where C and C_o are the solids contents of the sample of skim and the uncreamed latex.

A calibration curve relating the size of creamed particles and the associated concentration of alginate can be constructed based on electron microscope measurements. An approximate equation expressing this relation has been determined:

$$d = 223 + \frac{111.7}{c_a}$$

where d is the particle diameter in Angstroms and c_a the concentration of alginate in per cent. A particle size distribution can be plotted from the values of M_α and d. This technique has been applied successfully to latexes based on 90:7.5:2.5 terpolymers of butyl acrylate:methyl methacrylate:methacrylamide (VII-17).

B. CHARACTERIZATION OF EMULSION POLYMERS

Although an extensive discussion is beyond the scope of this bulletin[a], a brief description of the more important facets of this subject may be helpful.

For the most part, the methods require previous isolation of the polymer from the latex. Of the many procedures for doing this, the following are most frequently used:

a. Coagulation with relatively small amounts of added mineral acids.

b. Coagulation with salts, especially those of polyvalent metals such as the alums.

c. Precipitation with solvents, usually methanol, isopropyl alcohol, acetone, etc. The selection of solvent depends on the nature of the polymer.

d. Freeze-drying techniques.

Combinations of these methods are often required in specific cases; the coagulated solids are usually collected, washed with water or solvents to remove surfactants, salts, unconverted monomers, and other impurities, and dried in air or under reduced pressure. For very exacting studies, the product may be further purified by solution in a suitable solvent and reprecipitation or freeze-drying.

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[a] A more complete outline of methods generally useful in the study of the properties and structure of polymers and pertinent reference material is given in the bulletin entitled "Characterization of Polymers" (SP-197) available from the Special Products Department.

1. MOLECULAR WEIGHT MEASUREMENTS AND SOLUTION VISCOSITIES

Several techniques are available for the determination of the various average molecular weights of polymers. The most commonly used method is viscometry from which M_v, the viscosity average molecular weight, can be calculated if a relationship to viscosity is known. Preferred solvents are those in which solvent-polymer interactions are not strong; these solvents include aromatic hydrocarbons, dioxane, and other liquids of low polarity. For copolymers, calculations of M_v are less reliable, but viscosity measurements can nevertheless be used for comparison of products having similar compositions. Simple viscosity measurements on concentrated solutions, from which M_v cannot be calculated with any high degree of confidence, serve for routine control and may indicate suitability for specific applications. For this type of measurement, a Brookfield viscosimeter, Gardner-Holdt tubes (ASTM 1725), or the bubble time method (ASTM D1545-60) are often adequate.

Osmometric data, which gives M_n, the number average molecular weight, are useful for many polymers and copolymers. The availability of commercial instruments, such as the Mechrolab Osmometer Model 501 (VII-e), has greatly increased the convenience of this approach. Weight average molecular weights, M_w, are obtained by light scattering techniques using a light scattering photometer (VII-f). To give meaningful results for copolymers, light scattering data on a series of solutions in as many as five solvents may be required (VII-18).

2. GLASS TRANSITION TEMPERATURE (T_g) AND RELATED PROCESSES

When amorphous polymers are passed through a relatively sharp temperature region which includes the so-called glass transition temperature T_g, they are changed from relatively hard brittle glasses to relatively soft viscous rubbers. Many properties of polymers undergo dramatic change around T_g; among these are thermal expansivity, torsional modulus, refractive index, dielectric properties, impact resistance, flow properties, load-bearing capacity, heat capacity, hardness, tackiness, and film-forming properties. Some of these changes can be used to locate the value of T_g. Table VII-1 lists some of the more useful methods for the measurement of T_g, the property observed, relevant ASTM methods when available, and helpful references. The values of T_g vary somewhat in accordance with the procedure used for their determination and are also affected by the time during which the changes are allowed to occur. The commonly accepted values are obtained by dilatometry; refractive index changes or strain gauge measurements give results agreeing closely with dilatometric values. Some methods give only approximations of the true values of T_g but are retained because of their experimental simplicity or usefulness in indicating utility in applications.

TABLE VII-1

METHODS OF MEASUREMENT OF T_g

Method	Property	ASTM	Reference
Dilatometry	Rate of Thermal Expansion	D-864	VII-19,20
Differential Pressure Transducer	Rate of Thermal Expansion		VII-21
Strain Gauge	Rate of Thermal Expansion		VII-22
Torsional Pendulum	Torsional Modulus	D-2236	VII-23,24,25
Torsional Braid	Torsional Modulus		VII-26,27
Refractometry	Refractive Index		VII-28,29
Dielectric	Dissipation Factor		VII-30,31
Brittle Point	Impact Resistance	D-1790	
Vicat	Flow	D-1525	

Approximate values of T_g for copolymers can be calculated from the values for the component homopolymers (in degrees Kelvin) by assuming a linear relation to the weight composition:

$$\frac{1}{T_g} = \frac{w_1}{T_{g_1}} + \frac{w_2}{T_{g_2}} + \ldots \frac{w_n}{T_{g_n}}$$

For example, T_g of a 40/60 (w/w) copolymer of ethyl acrylate (T_g = -22°C) and methyl methacrylate (T_g = 105°C) may be computed as follows:[a]

$$\frac{1}{T_g} = \frac{0.40}{(273-22)} + \frac{0.60}{(273+105)} = 0.00317$$

$$T_g = 42°C. \text{ or } 315°K.$$

The assumption underlying the above equation holds well for most all-acrylic copolymers and for some other copolymers. As might be expected, deviations from linearity have been observed in certain copolymer systems. Among these are the copolymers of methyl methacrylate with styrene or acrylonitrile which show minimum T_g/composition values at 90°C. (35% ester content) and 80°C. (65% ester content) respectively and vinylidene chloride-methyl acrylate with a maximum of 50°C. for 50/50 mixtures. It is possible that other deviants may be disclosed by future investigations.

The glass temperature of an amorphous polymer is one of the key parameters which often determines its utility. For example, when a thermoplastic material is needed for an application requiring high strength, rigidity, and hardness, a material with high T_g used in the glassy region would be indicated; such a material among the acrylic polymers is poly(methyl methacrylate). A permanent adhesive or sealant, having high flexibility, tackiness, and softness would call for a polymer having a low T_g to be used in its rubbery region; poly(butyl acrylate) is such a material. T_g also aids in specifying compositions of film-formers; in making a selection of such compositions, the conditions under which they are applied to a substrate as well as their properties under ambient conditions should be considered.

3. MINIMUM FILM-FORMING TEMPERATURE (MFT)

When a polymer emulsion is spread over a substrate and allowed to evaporate, the residual polymer may or may not coalesce into a continuous film, depending on its deformability and the temperature (VII-32). Continuous films are obtained at a temperature near T_g, or more precisely, above the minimum film-forming temperature (MFT). MFT may differ somewhat from T_g because of the plasticizing action of water and soaps contained in the polymer particles and is usually somewhat lower (VII-33). MFT may also be somewhat higher on porous than on non-porous substrates (VII-21). Below MFT, powdery or cheesy compositions of little strength are produced.

A convenient laboratory instrument[b] has been developed by which MFT may be determined quickly and reproducibly with a precision of a few degrees (Figures 8, 9, 10,11). This

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[a] A pocket-size Acrylic Glass Temperature Analyzer (SP-222) is available from the Special Products Department. The Analyzer lists factors for acrylic and other common monomers by which T_g of copolymers can be conveniently computed with the elimination of most of the arithmetical operations.

[b] A description of the instrument and its operation is given in Special Products Department Bulletin SPR-298.

FIGURE 8

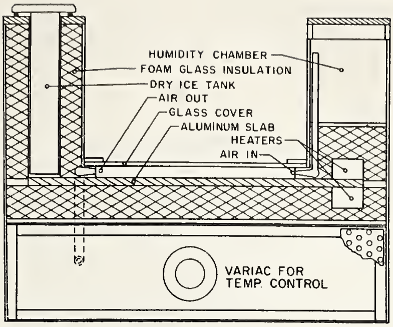
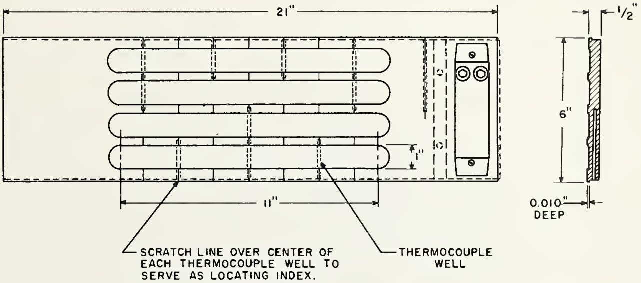
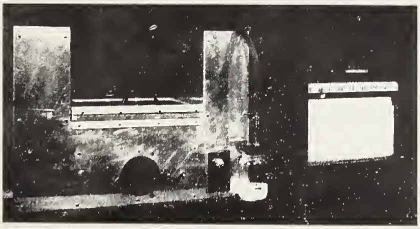


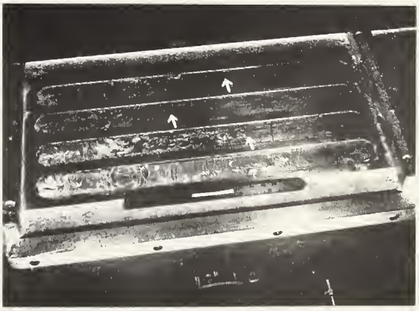
FIGURE 9





Minimum film temperature apparatus.

FIGURE 10



Test slab showing typical films formed from polymer emulsions. Points of transition from continuous to discontinuous film indicated by arrows.

FIGURE 11

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apparatus can be used for measurements between 0 and 100°C., the practical limits resulting from the freezing and boiling points of water. Means are also provided to control the humidity above the films if simulation of the effect of atmospheric moisture on the rate of film formation is desired.

4. EVALUATION OF PERFORMANCE CHARACTERISTICS AND FILM PROPERTIES OF FORMULATED EMULSIONS

Acrylic polymer emulsions are frequently modified by mixture with other substances such as pigments, surfactants, other emulsions, etc., to furnish products suitable for applications. A discussion of the production and evaluation of such products is beyond the scope of this bulletin. However, there are many comprehensive reviews and papers on the formulation of specific emulsion polymers and the properties of the resulting materials. The Special Products Department will gladly furnish assistance in the location of reference publications on the use of acrylic emulsion polymers in specific applications.

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(VII-a) George D. Ellis and Sons, American & Luzerne Sts., Philadelphia, Pa. 19140.

(VII-b) A. H. Thomas Co., Catalog #2354, Philadelphia, Pa. 19107.

(VII-c) Carl Zeiss Inc., New York, N. Y. 10018.

(VII-d) Spinco Division, Beckman Instruments Co., Palo Alto, Calif.

(VII-e) Mechrolab Co., Mountain View, Calif.

(VII-f) Phoenix Precision Instrument Co., Philadelphia, Pa. 19140.

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